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WATER NUTRIENTS NUMBER 1

Raymond J. Lishka, et al

Environmental Control Administration
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WATER NUTRIENTS NO. 1

Study Number 27

Report of a Study Conducted by the
ANALYTICAL REFERENCE SERVICE

Raymond J. Lishka, Laurella A. Lederer, and Earl F. McFarren
TRAINING PROGRAM
National Center for Urban and Industrial Health

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Bureau of Disease Prevention and Environmental Control
Cincinnati, Ohio
1966

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FOREWORD

The Analytical Reference Service (ARS) is conducted by the Training Program of the National Center for Urban and Industrial Health to evaluate laboratory methods in the environmental field. Cooperative studies by member organizations, who analyze identical samples and critically review methodology, provide the mechanism for:

Evaluation of analytical procedures, including precision and accuracy, by comparison of the procedures and results reported by participating laboratories.

Exchange of information regarding method characteristics.

Improvement or replacement of existing methods by development of more accurate procedures, and development of new methodology for determination of new polluttional compounds.

Samples are designed to contain measured amounts of selected constituents. Decisions as to qualitative makeup are made by the ARS staff, the membership, and consultants. Notice of each study is sent to the entire membership.

To those who desire to participate, a portion of the study sample is sent, along with data forms for reporting numerical values, a critique of the procedures used, comments on modifications, sources of error, difficulties encountered, or other pertinent factors. The results and comments received are compiled, and a report of each study is prepared.

Initially directed toward examination of water, studies now include air, milk, and food. Some studies are periodically repeated for the advantage of new members, to evaluate new methods, or to reevaluate existing methods.

The selection of studies is guided by the responses to questionnaires periodically circulated among the membership, which now includes 304 Federal, state, and municipal agencies; industries; universities; consulting firms; and foreign agencies.

James P. Sheehy
Chief, Training Program

ACKNOWLEDGMENTS

Michael J. Taras, Chairman, Joint Editorial Board on Standard Methods for the Examination of Water and Wastewater suggested that this study be undertaken because of the need for data on the precision and accuracy of the methods for analysis of certain nutrients, which occur in the 12th edition of that publication.

D.G. Ballinger, Technical Advisory and Investigations Activities, J.M. Cohen, Basic and Applied Sciences Section, and A.W. Breidenbach and R.C. Kroner, Water Quality Activities - all of the Federal Water Pollution Control Administration - commented upon the proposed samples and suggested some improvements in the design of the study and composition of the samples.

J.F. Santner, Mathematical Sciences, Office of the Director, assisted in the development and testing of methods for rejection of outliers.

Paul W. Britton, Computer Sciences, Office of the Director, assisted in the development of computer programs for statistically analyzing the data.

J.M. Matthews, Chemist, Analytical Reference Service, prepared the samples and checked the accuracy and stability of the samples by performing many analyses of aliquots of the samples both before and after distribution.

STUDIES COMPLETED AND REPORTED

Water-Minerals	Calcium, magnesium, hardness, sulfate, chloride, alkalinity, nitrite, nitrate, sodium, and potassium. Studies completed in 1956, 1958, and 1961.
Water-Metals	Lead, copper, cadmium, aluminum, chromium, iron, manganese, and zinc. Studies completed in 1957 and 1962. These same metals plus silver. Study completed in 1965.
Water-Fluoride	Fluoride in the presence and absence of interferences, with and without distillation by a specified procedure. Studies completed in 1958 and 1961.
Water-Radioactivity	Gross beta activity. Studies completed in 1959 and 1961. Gross beta and strontium-90 activity. Study completed in 1963.
Water-Surfactant	Surfactant in various waters. Studies completed in 1959 and 1963.
Water-Oxygen Demand	Biochemical oxygen demand and chemical oxygen demand. Study completed in 1960. Chemical oxygen demand. Study completed in 1965.
Water-Trace Elements	Arsenic, boron, selenium, and beryllium. Study completed in 1962. These same metals plus vanadium. Study completed in 1966.
Freshwater Plankton	Evaluation of the precision and accuracy obtainable by the use of various methods of plankton counting and identification. Study completed in 1964.
Water-Nutrients	Silicate, phosphate, nitrate nitrogen, organic nitrogen and ammonia nitrogen. Study completed in 1966.
Air-Inorganics	Chloride, sulfate, fluoride, and nitrate in aqueous solution and on glass-fiber high-volume filter mats. Study completed in 1958.

Air-Lead	Filter paper tape impregnated with lead. Study completed in 1961.
Air-Particulates	Microscopic identification of some common atmospheric particulates. Study completed in 1964.
Air-Sulfur Dioxide	Sulfur dioxide in air by a specified method. Study completed in 1963.
Water-Pesticides	Lindane, heptachlor epoxide, DDE, and dieldrin in water. Study completed in 1965.
Food-Pesticides	DDT in milk. Study completed in 1962. Lindane, heptachlor epoxide, DDE, and dieldrin in food. Study completed in 1965.

PARTICIPANTS IN THIS STUDY

Alexander Orr Jr. Water Treatment Plant, Miami, Florida
Anaconda Company, Grants, New Mexico
Atomic Energy Research Establishment, Didcot, Berks, England
Bender Hygienic Laboratory, Albany, New York
Bio-Technics Laboratories, Incorporated, Los Angeles, California
Brown & Caldwell Laboratories, San Francisco, California
Calgon Corporation, Pittsburgh, Pennsylvania
California Department of Water Resources, Riverside
California Department of Water Resources, Sacramento
California Department of Water Resources, San Bernardino
California State Department of Public Health, Berkeley
California State Department of Public Health, Los Angeles
California Water Service Company, San Jose
Central District Filtration Plant, Chicago, Illinois
Colorado Department of Public Health, Denver
Connecticut State Department of Health, Hartford
Department of Energy, Mines & Resources, Ottawa, Ontario, Canada
DHEW, PHS, Food Chemistry, Cincinnati, Ohio
Department of Municipal Laboratories, Hamilton, Ontario, Canada
Department of National Health and Welfare, Ottawa, Ontario, Canada
Department of National Health and Welfare, Vancouver, Canada
Division of Water Pollution Control, Cincinnati, Ohio
Dow Chemical Company, Midland, Michigan
Drexel Institute of Technology, Philadelphia, Pennsylvania
Easterly Pollution Control Center, Cleveland, Ohio
Fairbank, Morse, and Company, Incorporated, Beloit, Wisconsin
Fresno Department of Public Health, California
Hammond-Montel, Incorporated, Elmhurst, New York
Holzmacher, McLendon & Murrell, Melville, New York
Houston Health Department, Texas
Hyperion Treatment Plant, Playa Del Rey, California
Idaho Department of Health, Boise
Illinois State Water Survey, Champaign
INFILCO, Division of Fuller Company, Tucson, Arizona
Iowa State Hygienic Laboratory, Des Moines
Iowa State University, Ames
Israel Institute of Technology, Haifa
Johns-Manville Research Center, Manville, New Jersey
Kansas State Department of Health, Topeka
Kem-Tech Laboratories, Incorporated, Baton Rouge, Louisiana
Lawrence Experiment Station, Massachusetts
Los Angeles County Flood Control District, California
Los Angeles Department of Water and Power, California
Louisiana State University, Analyst A, Baton Rouge

Louisiana State University, Analyst B, Baton Rouge
 Manhattan College, Bronx, New York
 Maryland State Department of Health, Baltimore
 Massachusetts Department of Public Health, Amherst
 Metropolitan Corporation of Greater Winnipeg, Manitoba, Canada
 Metropolitan Utilities District, Omaha, Nebraska
 Michigan Department of Health, Lansing
 Minneapolis Water Department, Minnesota
 Monroe County Department of Health, Rochester, New York
 Nassau County Department of Health, Hempstead, New York
 Nevada State Health Division, Reno
 New Hampshire Water Pollution Commission, Concord
 New York State Conservation Department, Scottsville
 New York State Department of Health, Analyst A, Albany
 New York State Department of Health, Analyst B, Albany
 New York State Department of Health, New Rochelle
 New York State Department of Health, Rochester
 New York State Department of Health, Syracuse
 North Carolina Department of Water Resources, Durham
 North Carolina Department of Water Resources, Raleigh
 Ohio Department of Health, Columbus
 Orange County Department of Agriculture, Anaheim, California
 Oregon State Sanitary Authority, Portland
 Pan American World Airways, Patrick Air Force Base, Florida
 Philadelphia Suburban Water Company, Bryn Mawr, Pennsylvania
 Pomeroy, Johnston & Bailey, Pasadena, California
 Procter & Gamble Company, Cincinnati, Ohio
 Ray W. Hawksley Co., Inc., Richmond, California
 Regional Environmental Health Lab (SGHK), Kelly AFB, Texas
 Research Institute for Public Health Engineering, Delft, Netherlands
 Rhode Island Department of Health, Providence
 Salem-Beverly Water Supply Board, Beverly, Massachusetts
 Scientific Research Council, Kingston, Jamaica, W.I.
 Swedish Water and Air Pollution Research Laboratory, Stockholm, Sweden
 Tennessee Valley Authority, Chattanooga
 Texas State Health Department, Austin
 U.S. Army Environmental Hygiene Agency, Edgewood Arsenal, Maryland
 USDI, FWPCA, Advanced Waste Treatment Activities, Cincinnati, Ohio
 USDI, FWPCA, Chemistry and Physics Activities, Cincinnati, Ohio
 USDI, FWPCA, Engineering Activities, Cincinnati, Ohio
 USDI, FWPCA, Great Lakes-Illinois River Basins Project, Chicago, Illinois
 USDI, FWPCA, Ohio River Basin Project, Wheeling, West Virginia
 USDI, FWPCA, Pacific Northwest Water Laboratory, Corvallis, Oregon
 USDI, FWPCA, Raritan Bay Project, Metuchen, New Jersey
 USDI, FWPCA, Southeastern Comprehensive Water Pollution Control
 Project, Atlanta, Georgia
 USDI, FWPCA, Technical Advisory and Investigations Activities,
 Cincinnati, Ohio

USDI, FWPCA, Water Quality Activities, Cincinnati, Ohio
USDI, Geological Survey, Columbus, Ohio
USDI, Geological Survey, Denver, Colorado
USDI, Geological Survey, Little Rock, Arkansas
USDI, Geological Survey, Sacramento, California
USDI, Geological Survey, Washington, D.C.
U.S. Industrial Chemicals Company, Tuscola, Illinois
Universidad Nacional de Colombia, Bogota, Colombia
University of California, Sanitary Engineering Research Laboratory,
Richmond
University of Florida, Gainesville
University of North Carolina, Chapel Hill
University of Wisconsin, Madison
Vermont Department of Health, Burlington
Vermont Department of Water Resources, Montpelier
Washington State Department of Health, Seattle
Washington State University, Pullman
Water Research Association, Marlow, Bucks, England
Water Service Laboratories, Incorporated, New York, New York
West Virginia Department of Natural Resources, Charleston
Wisconsin Laboratory of Hygiene, Madison

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ABSTRACT

In this study, three concentrated solutions were shipped in sealed glass ampoules with instructions to dilute 5 ml of each sample to 1 liter. The diluted solutions contained different mixtures of silica, phosphate, nitrate nitrogen, ammonia nitrogen, and organic nitrogen at concentrations commonly found in water analysis. The results indicate that many analysts failed to include molybdate-unreactive silica in a total silica measurement and polyphosphates in a total phosphate analysis. The best silicate results were obtained using the colorimetric molybdosilicate method, and the best phosphate, by the stannous chloride method. Nitrate analysis was most frequently performed using phenoldisulfonic acid, which produced the least accurate results. The best results were obtained with the modified brucine method, although nearly equal accuracy and precision were produced by the chromotropic acid method. All nitrate methods failed to produce accurate results in the presence of moderately high chlorides. The determination of ammonia by direct nesslerization and autoanalyzer (except at the lower concentration) produced good accuracy and precision in samples containing no interferences, but distillation introduced substantial error. The measurement of organic nitrogen is not very accurate, regardless of method used. At a concentration of 0.20 mg/liter of organic nitrogen, all methods were unacceptable.

WATER NUTRIENTS NO. 1

PURPOSE OF THE STUDY

Nutrients in water are important because they promote biological responses that may interfere with some desired use of the water by man. Algae, bacteria, fungi, and aquatic plants are the forms of life that nutrients affect most directly.

Silicon is an important element in algal growth and especially important in the population growth of diatoms. Phosphate occurs in traces in many natural waters, and often in appreciable amounts during periods of low biologic productivity. Traces of phosphate increase the tendency of troublesome algae to grow in reservoirs.

Nitrogen can be taken up by most algae as either ammonium salts or as nitrates. Supplementary amines are required by certain varieties of algae.

Analysis of the various forms of these nutrients is routine in many laboratories, but the reliability of the results obtained has been questionable.

This study was designed to evaluate the precision* and accuracy* of the commonly used analytical methods for the measurement of silica, phosphate, nitrate nitrogen, ammonia nitrogen, and organic nitrogen.

DESIGN OF THE STUDY

The water samples were prepared as concentrated solutions to ensure greater stability of the samples and to reduce shipping costs. Participants were instructed to dilute 5 ml of each sample to 1 liter. The solutions were shipped in sterile, sealed glass ampoules and consisted of sterile, distilled, deionized water containing the compounds indicated in Table 1.

The chloride was added as an interference in the nitrate determination and, hence, no chloride analysis was requested. The pH of each concentrated sample was adjusted to below 1.5 with sulfuric acid to preserve the sample.

Accompanying the announcement letter of this study was a survey form on which participants were requested to indicate the analytical method they would use for each determination. The purpose was to ensure an adequate

* These terms are defined in Appendix B.

number of analyses by each method to provide valid statistical evaluation of the methods. A copy of the survey form returned by the participant was sent with the sample as a reminder to the participant to use the methods indicated. Unfortunately, a number of participants used methods other than those they had previously indicated. In several cases, the use of a relatively unknown method by only one participant made evaluation of that procedure impossible. Furthermore, some participants used the method they had previously indicated, but added modifications of their own and, in effect, created a different procedure which again could not be adequately evaluated because only a single result was available.

Table 1. Composition of Samples

Compound	Nutrient	Nutrient in diluted sample, mg/liter		
		Sample 1	Sample 2	Sample 3
$\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$	SiO_2	5.0	15.0	30.0
$(\text{NaPO}_3)_6$	PCl_4	10.00	5.00	0.50
KNO_3	N (nitrate)	1.00	1.00	1.00
NH_4Cl	N (ammonia)	0.20	0.80	1.50
Glutamic acid	N (organic)	1.50	0.80	0.20
NaCl	Cl^- interference	10.00	200.00	400.00

It is recognized that the analyst hopes to achieve greater accuracy by using a method he considers superior, but in so doing, he is defeating the primary purpose of the study, which is the evaluation of a specific method. Of course, data obtained by other methods are always welcome and sometimes provide useful information; often, however, they are of no value, particularly if only one participant submits data by that method. If the participant is to make a worthwhile contribution, he should analyze the sample by both methods, the designated method and the method of his choice, and submit both sets of data.

Several participants overlooked the request for a single analysis and submitted an average of several analyses. The statistical significance of these results obviously differs from the results obtained from a single analysis and makes interpretation of the data more difficult.

TREATMENT OF THE DATA

As the results of analysis were received from each participant, the data were reviewed, and in case of a suspected mathematical error the

reporting laboratory was asked to check its calculations and to submit a corrected value if an error was found.

The data were coded, key-punched on cards, and analyzed by electronic computer (described in Appendix A) for normality of distribution and subsequent rejection of outliers that were nonrepresentative because of errors in calculation, dilution, or other indeterminate factors. The rejection of outliers was performed separately on the results obtained by each method, and again collectively on all of the results regardless of method. In some cases, values that were rejected when considered according to method were retained in the overall computation; thus, the number of overall results does not always agree with the sum of the number of results considered by the individual methods. The previously used technique of plotting the data on probability paper to determine outliers was also used in this study to verify the initial computer program. The data were then statistically analyzed by computer for precision and accuracy.

Bar graphs are included in the text to provide a pictorial display of the data. Rejected values are indicated by an "m" for method grouping and an "o" for overall; broken bars indicate that the value is beyond the scale of the chart.

Analytical results received after statistical analysis was begun are not shown in this report.

DISCUSSION

SILICA (Tables 2-4, Figures 1-6)

This portion of the study was designed to evaluate the colorimetric molybdosilicate method⁽¹⁾ and the colorimetric heteropoly blue method⁽⁴⁾ appearing in the 12th edition of Standard Methods for the Examination of Water and Wastewater (SMEWW). The conditions present in the sample converted most of the silica to a molybdate-unreactive state; therefore, digestion with sodium bicarbonate became a necessary step if total silica was to be measured. The majority of participants chose to omit the digestion because the samples appeared to contain no insoluble material; and as a consequence, they obtained very low results. It is interesting to note that the molybdate-reactive concentration seemed to be about the same (slightly more than 1 mg/liter) in all three samples, whereas the total silica content was quite different.

The mean of the results obtained by the heteropoly blue method shows better accuracy for all three samples, although the precision and accuracy were slightly better for the molybdosilicate method on samples 1 and 2.

Table 2. SUMMARY OF DATA ON SILICA

Sample 1 (5.0 mg/liter added)

Method	Outliers not included	Number of results included	Mean	Mean error	Standard deviation	95% tolerance limits	Relative standard deviation	Relative error
Molybdosilicate, SMEWW	1	19	4.6	-0.4	0.66	± 1.84	14.3	8.0
Molybdosilicate, SMEWW ^a		26	1.4	-3.6	0.87	± 2.27	62.6	72.0
Heteropoly Blue, SMLWW		11	4.8	-0.2	1.32	± 4.30	27.2	4.0
Heteropoly Blue, SMEWW ^a	1	13	1.3	-3.7	0.25	± 0.77	15.2	74.0
Autoanalyzer ^a		3	1.3	-3.7	0.21	± 2.08	16.4	74.0
Molybdate Blue, USGSA		1	1.4	----	----	----	----	----
Morrison and Wilson ^a		1	1.2	----	----	----	----	----
Gravimetric, SMEWW		1	2.0	----	----	----	----	----
Overall (digested)		32	4.5	-0.5	1.21	± 3.05	26.9	10.0
Overall ^a	7	38	1.2	-3.8	0.20	± 0.49	15.8	76.0

^a Digestion step omitted.

Table 3. SUMMARY OF DATA ON SILICA

Sample 2 (15.0 mg/liter added)

Method	Outliers not included	Number of results included	Mean	Mean error	Standard deviation	95% tolerance limits	Realitive standard deviation	Relative error
Molybdosilicate, SMEWW	1	19	14.4	- 0.6	1.20	± 3.35	8.4	4.0
Molybdosilicate, SMEWW ^a		26	1.2	-13.8	0.43	± 1.12	35.0	92.0
Heteropoly Blue, SMEWW		11	15.4	+ 0.4	2.78	± 9.05	18.0	2.6
Heteropoly Blue, SMEWW ^a		14	1.3	-13.7	0.43	± 1.30	33.4	91.3
Autoanalyzer ^a		3	1.5	-13.5	0.53	± 5.26	35.2	90.0
Molybdate Blue, USGS ^a		1	1.1	-----	-----	-----	-----	-----
Morrison and Wilson ^a		1	1.1	-----	-----	-----	-----	-----
Gravimetric, SMEWW		1	11.0	-----	-----	-----	-----	-----
Overall (digested)		32	14.8	- 0.2	2.16	± 5.46	14.6	1.3
Overall ^a		45	1.3	-13.7	0.42	± 1.01	33.6	91.3

^a Digestion step omitted.

Table 4. SUMMARY OF DATA ON SILICA

Sample 3 (30.0 mg/liter added)

Method	Outliers not included	Number of results included	Mean	Mean error	Standard deviation	95% tolerance limits	Relative standard deviation	Relative error
Molybdosilicate, SMEWW		20	27.0	- 3.0	2.09	± 5.74	7.7	10.0
Molybdosilicate, SMEWW ^a	1	25	1.2	-28.8	0.57	± 1.50	49.1	96.0
Heteropoly Blue, S ^m EW	1	10	28.5	- 1.5	1.38	± 4.68	4.9	5.0
Heteropoly Blue, SMEWW ^a	1	13	1.2	-28.8	0.35	± 1.08	29.2	96.0
Autoanalyzer ^a		3	1.8	-28.2	0.78	± 7.73	43.4	94.0
Molybdate Blue, USGS ^a		1	0.8	-----	-----	-----	-----	-----
Morrison and Wilson ^a		1	1.1	-----	-----	-----	-----	-----
Gravimetric, SMEWW		1	25.0	-----	-----	-----	-----	-----
Overall (digested)	1	31	27.4	- 2.6	2.00	± 5.06	7.3	8.6
Overall ^a	2	43	1.2	-28.8	0.53	± 1.28	43.8	96.0

^a Digestion step omitted.

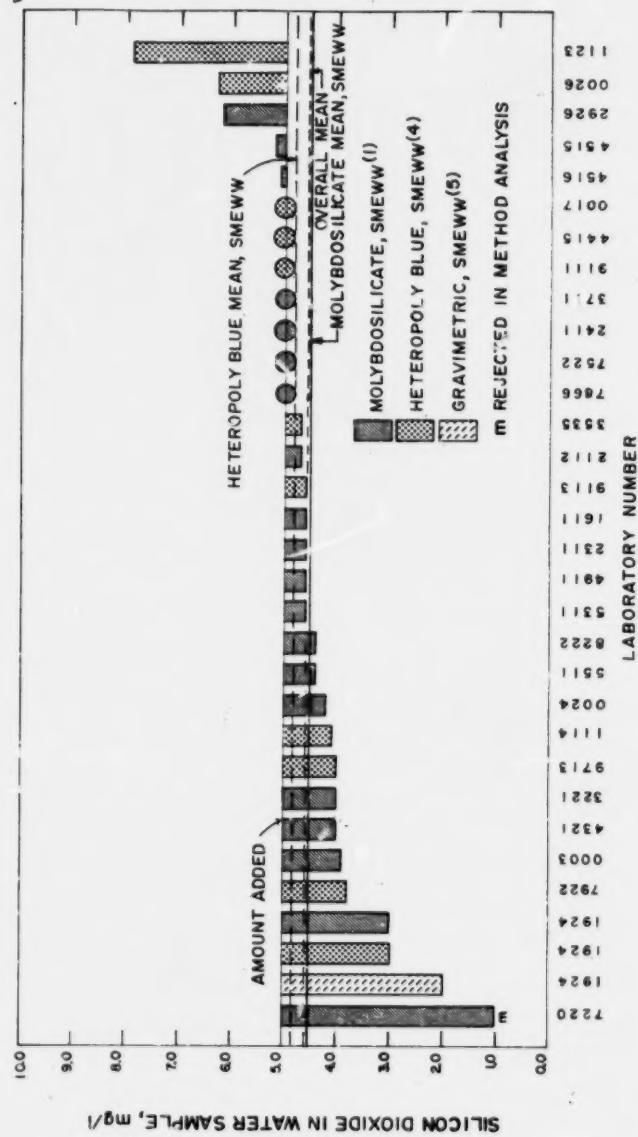


Figure 1. Bar graph for total silica in sample 1.

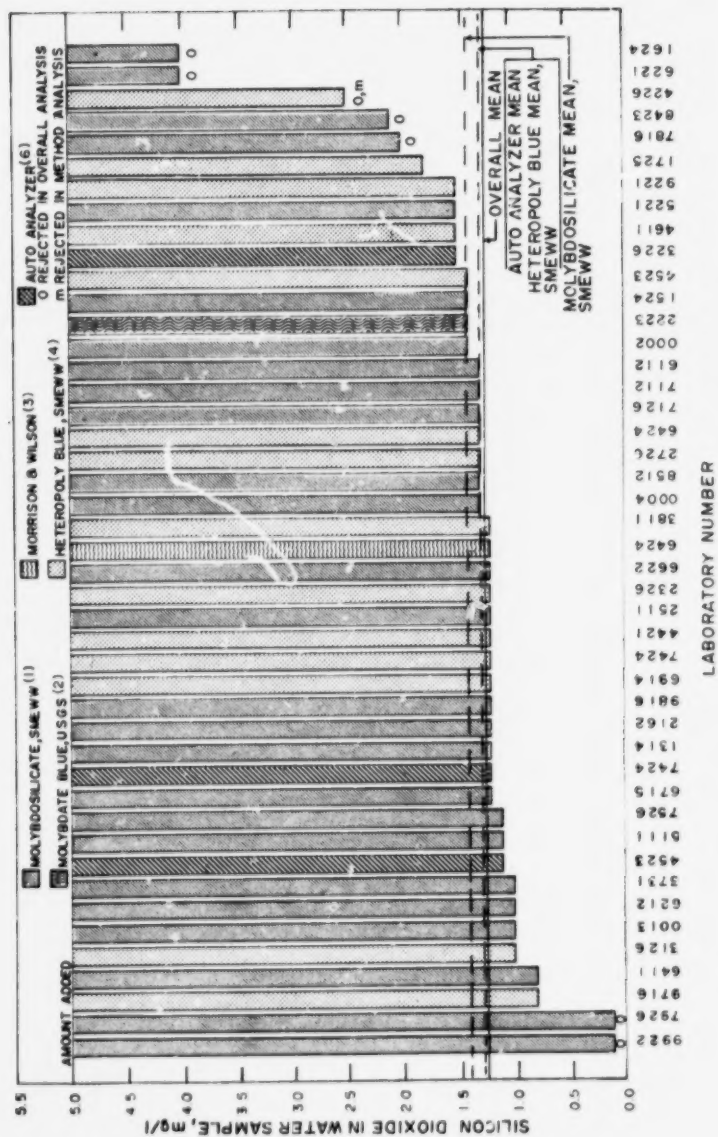


Figure 2. Bar graph for molybdate-reactive silica in sample 1.

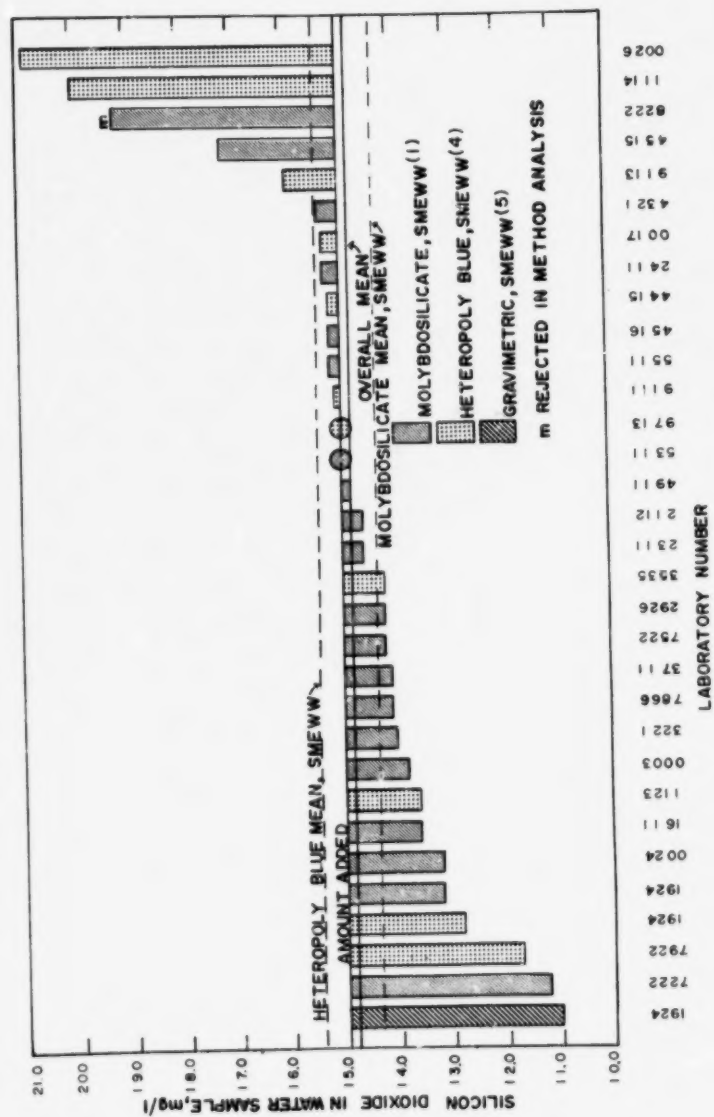


Figure 3. Bar graph for total silica in sample 2.

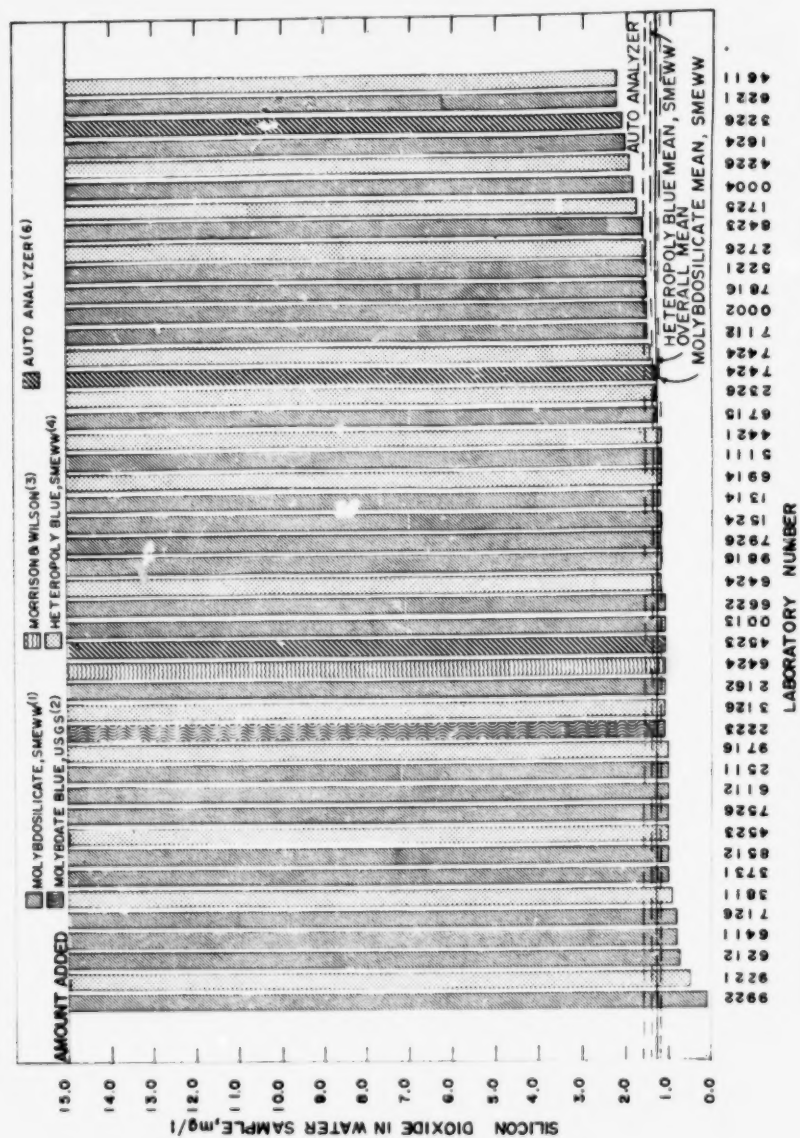


Figure 4. Bar graph for molybdate-reactive silica in sample 2.

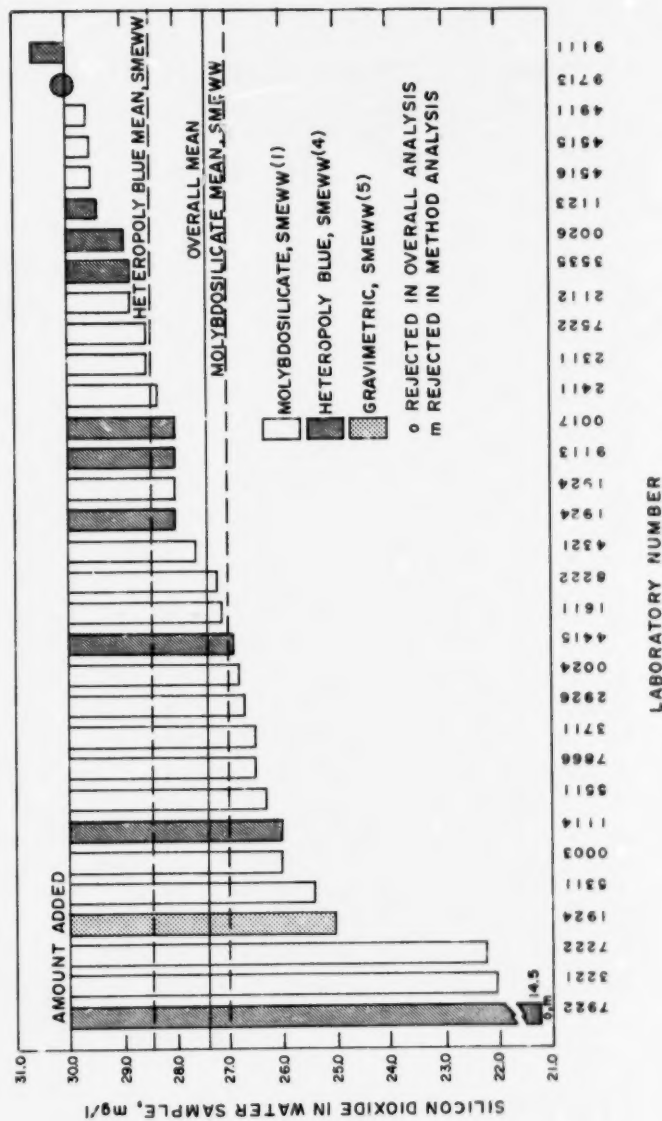


Figure 5. Bar graph for total silica in sample 3.

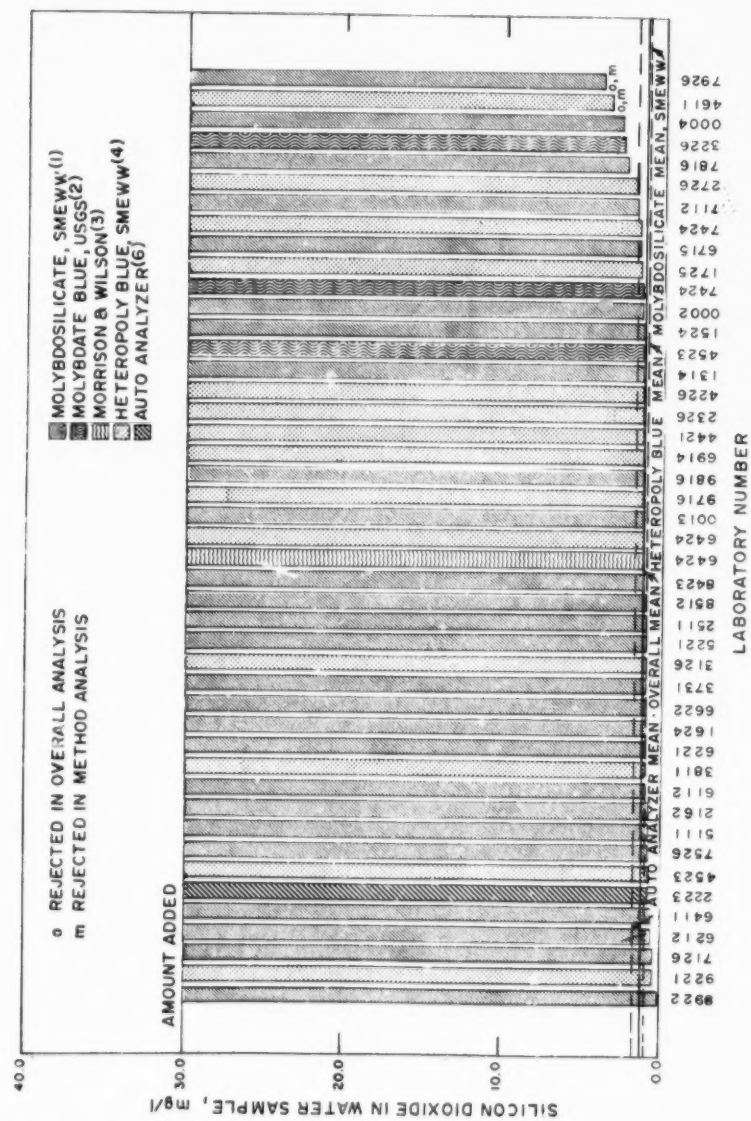


Figure 6. Bar graph for molybdate-reactive silica in sample 3.

A dramatic improvement in precision of the heteropoly blue method with increasing concentration is shown by the relative standard deviation. On the other hand, the mean error shows very little variation of accuracy with concentration, the mean of the results being within approximately 4 percent of the correct value in all three samples.

There does not appear to be a significant difference between the two methods when applied to this type of sample, which contained only phosphate as a potential interference. The items of greatest interest are the obvious need for the bicarbonate digestion if a total dissolved silica measurement by either method is desired and the poor results obtained in measuring the lower concentration (0.5 mg/liter) by the heteropoly blue method. Also evident is the analyst's inability to judge by visual inspection of the sample whether the silica is in a molybdate-reactive form. No evaluation of the autoanalyzer can be made since none of the analysts using automated analysis performed the bicarbonate digestion.

The ARS staff observed that in the digestion procedure best results were obtained if the samples were not placed too deep in the steam bath and evaporation of the samples was kept to a minimum.

TOTAL PHOSPHATE (Tables 5-7, Figures 7-15)

The purpose of phosphate analysis was to evaluate the aminonaphtholsulfonic acid⁽¹¹⁾ method and the stannous chloride method, with⁽¹⁵⁾ and without⁽⁷⁾ extraction. Total phosphate analysis⁽⁸⁾ was specifically requested because an evaluation of the complete procedure, including the hydrolysis step, was desired. The sample was spiked with a polyphosphate, which was partially hydrolyzed to orthophosphate by the acid used to preserve the samples. Almost half of the participants neglected to perform the hydrolysis and, consequently, obtained low results, regardless of method used.

The stannous chloride method without extraction was the most popular method and showed the best accuracy for all samples, as indicated by the close agreement between the mean and the amount added (mean error). The precision, as indicated by the relative standard deviation, was best for the stannous chloride method on the lower concentrations, but on the sample of high concentration (10 mg/liter) the aminonaphtholsulfonic acid method was more precise, but less accurate. The results obtained by six participants using the stannous chloride method with extraction were widely scattered for the samples of lower concentration. The autoanalyzer used by five participants, produced generally good results except for the lowest concentration sample, where precision dropped.

Table 5. SUMMARY OF DATA ON PHOSPHATE

Sample 1 (10.0 mg/liter added)

Method	Outliers not included	Number of results included	Mean	Mean error	Standard deviation	95% tolerance limits	Relative standard deviation	Relative error
Stannous Chloride, SMEWW	3	33	9.50	-0.50	0.816	±2.05	8.5	5.0
Stannous Chloride, SMEWW ^a	2	26	9.05	-0.95	0.574	±1.49	6.3	9.5
Aminonaphtholsulfonic acid, SMEWW	2	18	9.16	-0.84	0.374	±1.05	4.0	8.1
Aminonaphtholsulfonic acid, SMEWW ^a	2	13	8.80	-1.20	0.845	±2.60	9.6	12.0
Stannous Chloride with extraction, SMEWW	2	4	9.19	-0.81	0.448	±2.85	4.8	8.1
Stannous Chloride with extraction, SMEWW ^a	1	5	8.14	-1.86	0.717	±3.64	8.8	18.6
Autoanalyzer	1	5	9.50	-0.50	0.401	±2.03	4.2	5.0
Autoanalyzer ^a		2	8.9	-1.10	0.000	0.00	0.0	11.0
Hickey		1	9.20	-----	-----	-----	-----	-----
Stannous Chloride, SEC		1	10.00	-----	-----	-----	-----	-----
Fogg and Wilkinson		1	9.00	-----	-----	-----	-----	-----
Phosphomolybdate for total phosphate, USGS		1	8.80	-----	-----	-----	-----	-----
Robertson		1	9.70	-----	-----	-----	-----	-----
Total phosphate, NWQN		1	9.40	-----	-----	-----	-----	-----
Phosphomolybdate for orthophosphate, USGS		1	8.30	-----	-----	-----	-----	-----
Overall	10	63	9.33	-0.67	0.446	±1.03	4.7	6.7
Overall ^a	4	49	8.88	-1.12	0.809	±1.93	9.1	11.2

^a Only orthophosphate determined because sample was not hydrolyzed.

Table 6. SUMMARY OF DATA ON PHOSPHATE
Sample 2 (5.0 mg/liter added)

Method	Outliers not included	Number of results included	Mean	Mean error	Standard deviation	95% tolerance limits	Relative standard deviation	Relative error
Stannous Chloride, SMEWW	3	33	4.61	-0.19	0.515	± 1.29	10.7	3.8
Stannous Chloride, SMEWW ^a		28	3.61	-1.39	0.940	± 2.42	26.0	27.6
Aminonaphtholsulfonic acid, SMEWW		20	4.79	-0.21	0.635	± 1.74	13.2	4.2
Aminonaphtholsulfonic acid, SMEWW ^a		15	3.56	-1.44	0.660	± 1.95	18.5	28.8
Stannous Chloride with extraction, SMEWW		6	6.07	+1.07	2.830	± 12.40	46.6	21.4
Stannous Chloride with extraction, SMEWW ^a		6	3.12	-1.08	1.300	± 5.77	41.9	37.6
Autoanalyzer		5	4.45	-0.55	0.168	± 0.85	3.7	11.0
Autoanalyzer ^a		3	3.30	-1.70	0.900	± 8.92	27.2	34.0
Hickey		1	4.80	-----	-----	-----	-----	-----
Stannous Chloride, SEC		1	5.00	-----	-----	-----	-----	-----
Fogg and Wilkinson		1	4.20	-----	-----	-----	-----	-----
Phosphomolybdate for total phosphate, USGS		1	4.70	-----	-----	-----	-----	-----
Robertson		1	5.35	-----	-----	-----	-----	-----
Total phosphate, NWQN		1	3.92	-----	-----	-----	-----	-----
Phosphomolybdate for orthophosphate, USGS		1	2.70	-----	-----	-----	-----	-----
Overall ^a	3	70	4.74	-0.26	0.627	± 1.44	13.2	5.2
Overall ^a		53	3.51	-1.49	0.901	± 2.13	25.6	28.8

^a Only orthophosphate determined because sample was not hydrolyzed.

Table 7. SUMMARY OF DATA ON PHOSPHATE
Sample 3 (0.5 mg/liter added)

Method	Outliers not included	Number of results included	Mean	Mean error	Standard deviation	95% tolerance limits	Relative standard deviation	Relative error
Stannous Chloride, SMEWW	3	32	0.52	+0.02	0.089	±0.25	13.1	4.0
Stannous Chloride, SMEWW ^a		28	0.37	-0.13	0.084	±0.21	22.7	26.0
Aminonaphtholsulfonic acid, SMEWW		20	0.65	-0.15	0.314	±0.88	48.3	30.0
Aminonaphtholsulfonic acid, SMEWW ^a		15	0.40	-0.10	0.070	±0.20	17.2	20.0
Stannous Chloride with extraction, SMEWW		6	0.76	-0.26	0.258	±1.14	33.9	52.6
Stannous Chloride with extraction, SMEWW ^a		6	0.33	-0.17	0.204	±0.90	62.1	34.0
Autoanalyzer		5	0.51	+0.01	0.195	±0.99	38.3	2.0
Autoanalyzer ^a		3	0.50	0.00	0.100	±0.99	20.0	0.0
Hickey		1	0.55	-----	-----	-----	-----	-----
Stannous Chloride, SEC		1	0.00	-----	-----	-----	-----	-----
Fogg and Wilkinson		1	0.45	-----	-----	-----	-----	-----
Phosphomolybdate for total phosphate, USGS		1	0.54	-----	-----	-----	-----	-----
Robertson		1	9.30	-----	-----	-----	-----	-----
Total phosphate, NW-QN		1	0.98	-----	-----	-----	-----	-----
Phosphomolybdate for orthophosphate, USGS		1	0.46	-----	-----	-----	-----	-----
Overall	3	69	0.58	+0.08	0.214	-0.42	37.1	16.0
Overall ^a	1	52	0.39	-0.11	0.090	±0.21	23.0	22.0

^a Only orthophosphate determined because sample was not hydrolyzed.

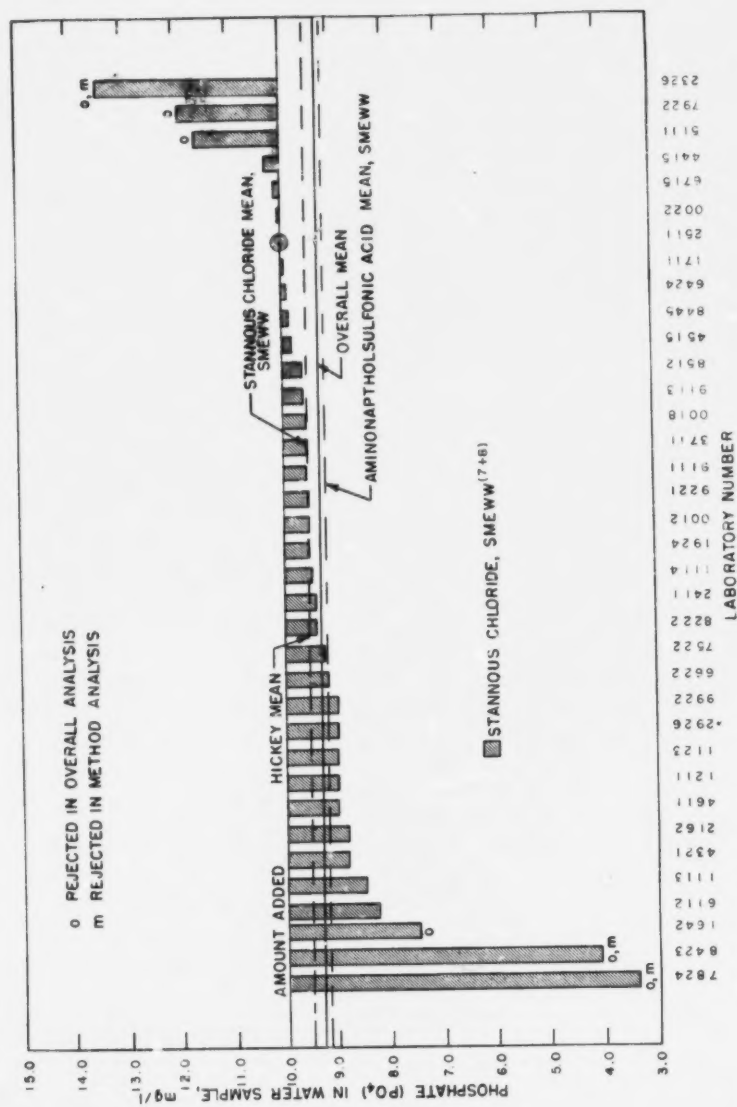


Figure 7. Bar graph for total phosphate in sample 1.

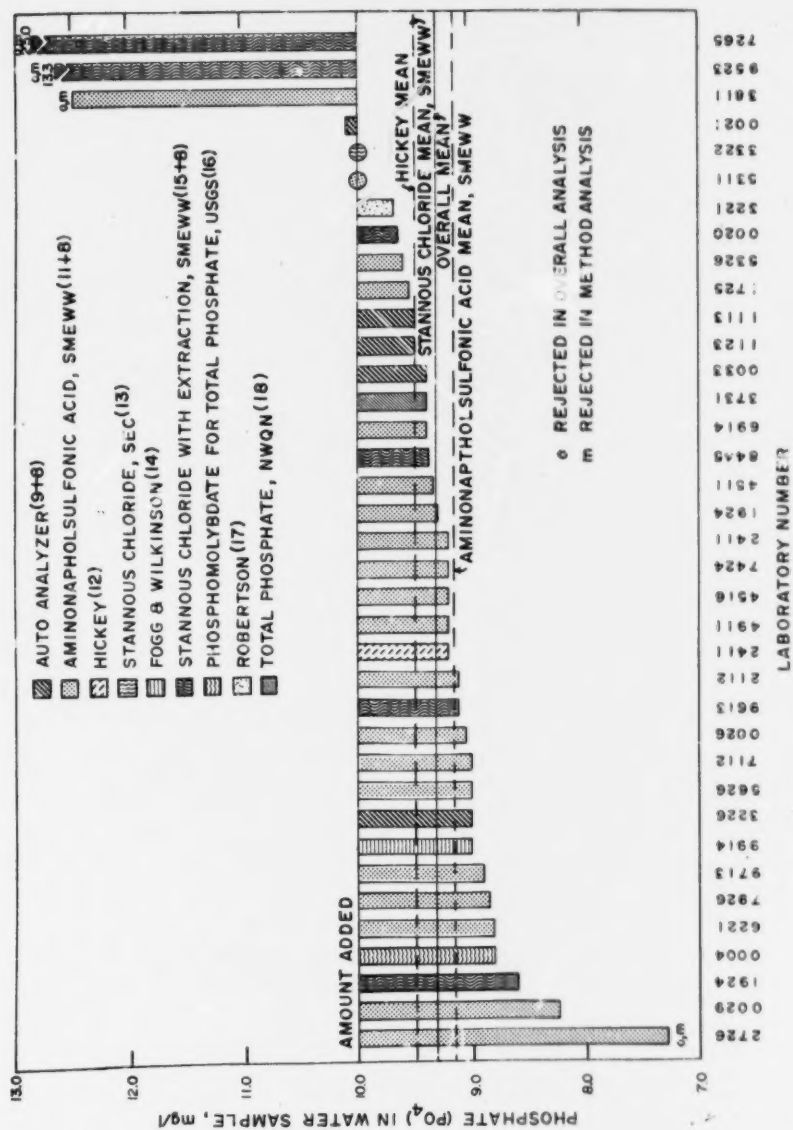


Figure 8. Bar graph for total phosphate in sample 1.

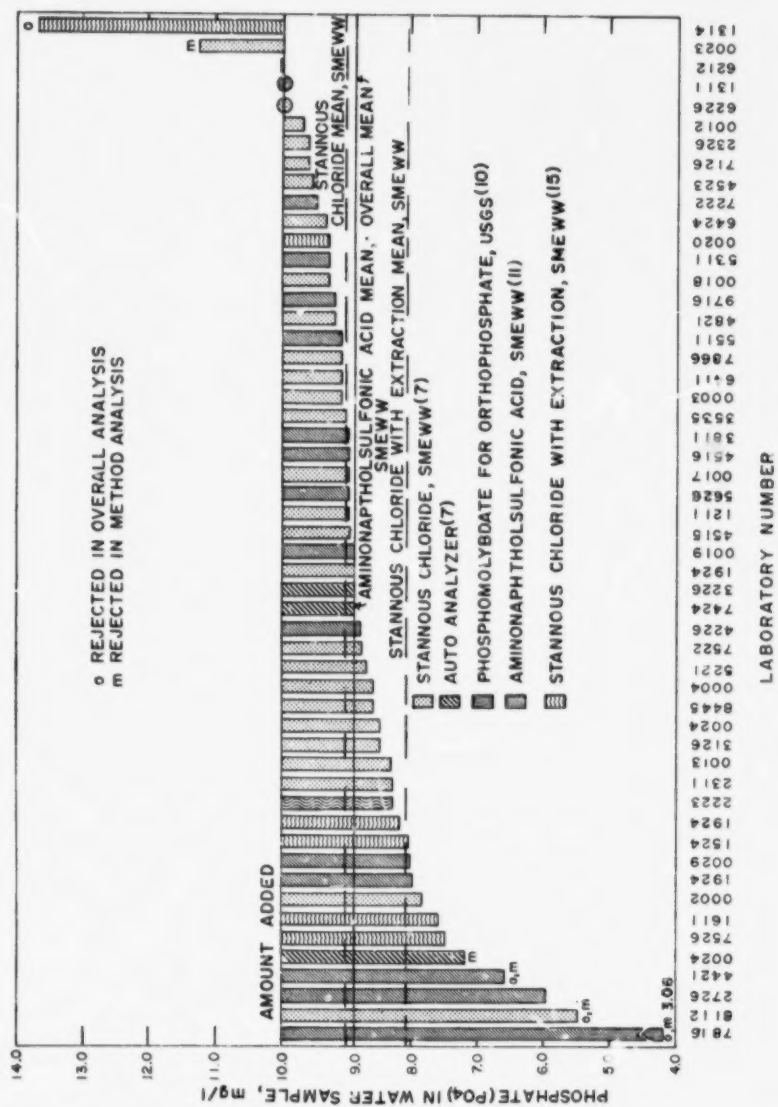


Figure 9. Bar graph for ortho phosphate in sample 1.

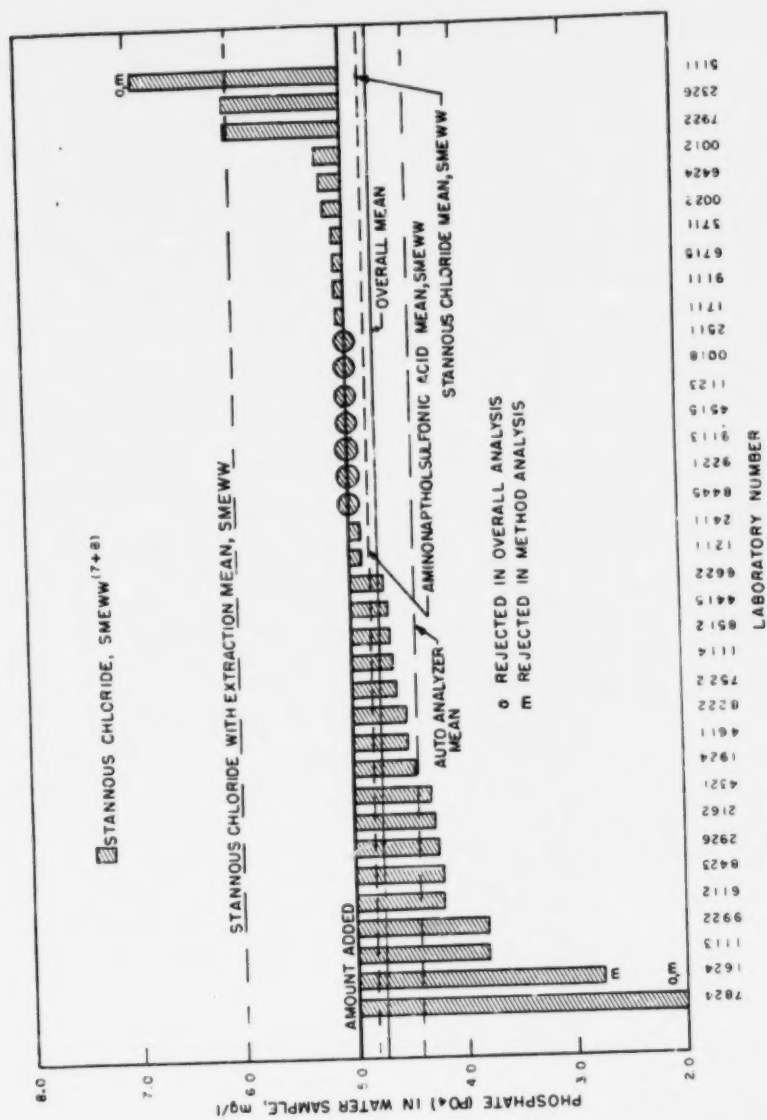


Figure 10. Bar graph for total phosphate in sample 2.

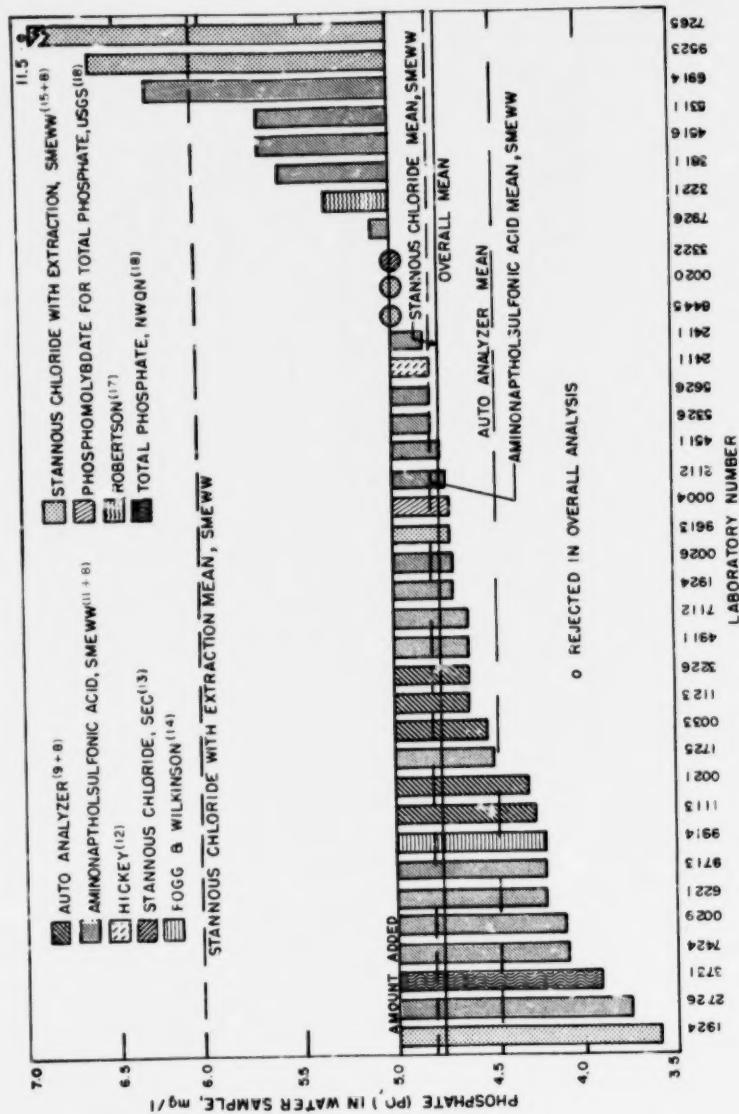


Figure 11. Bar graph for total phosphate in sample 2.

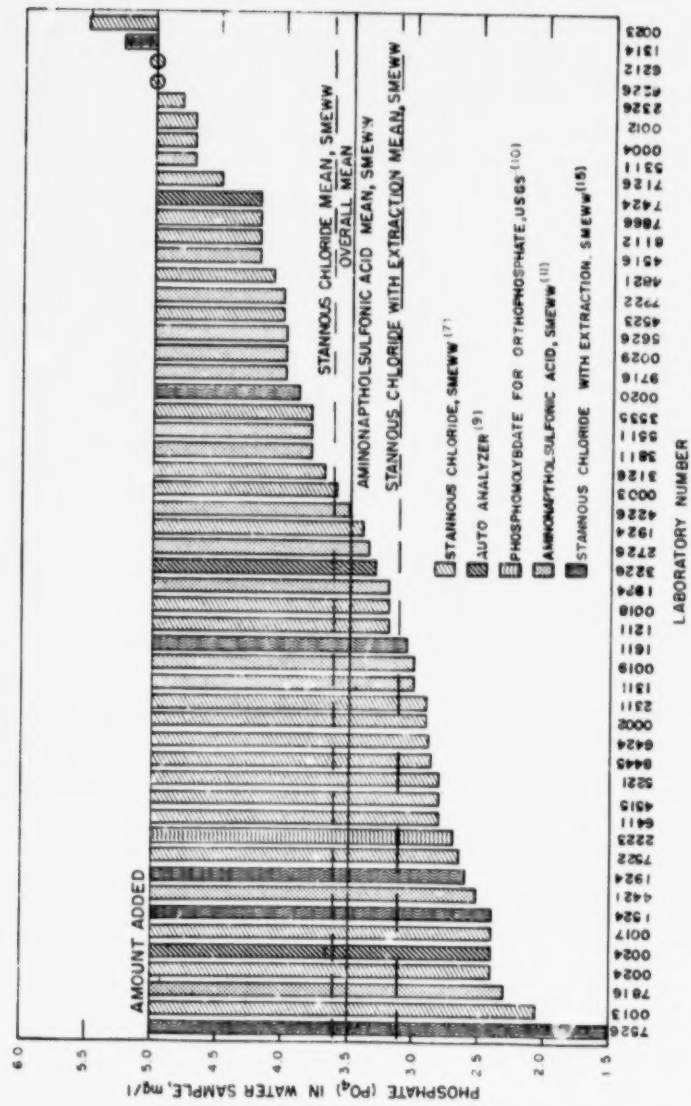


Figure 12. Bar graph for ortho phosphate in sample 2.

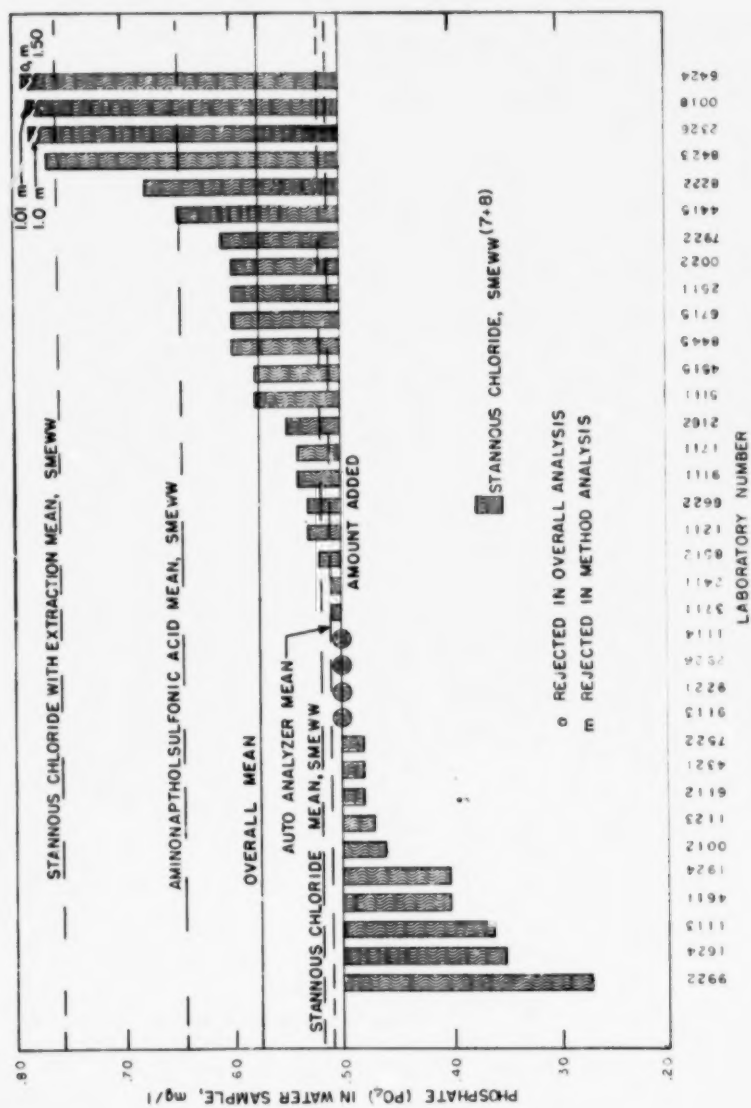


Figure 13. Bar graph for total phosphate in sample 3.

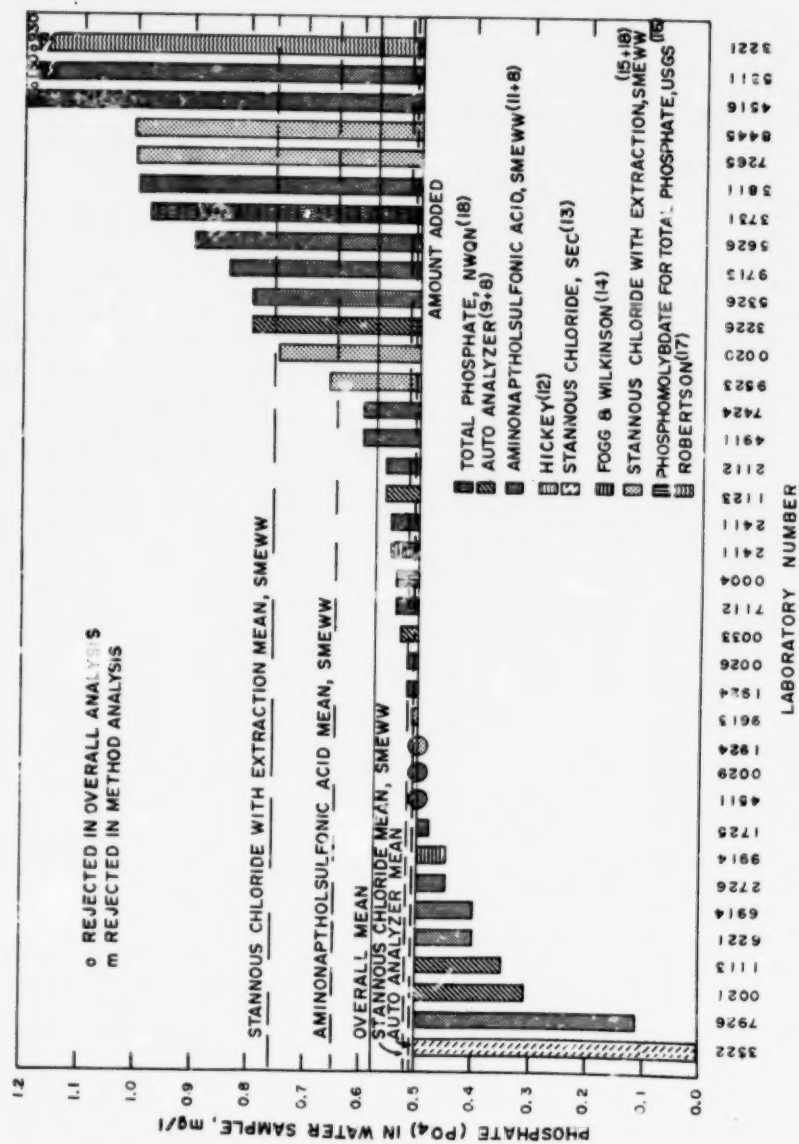


Figure 14. Bar graph for total phosphate in sample 3.

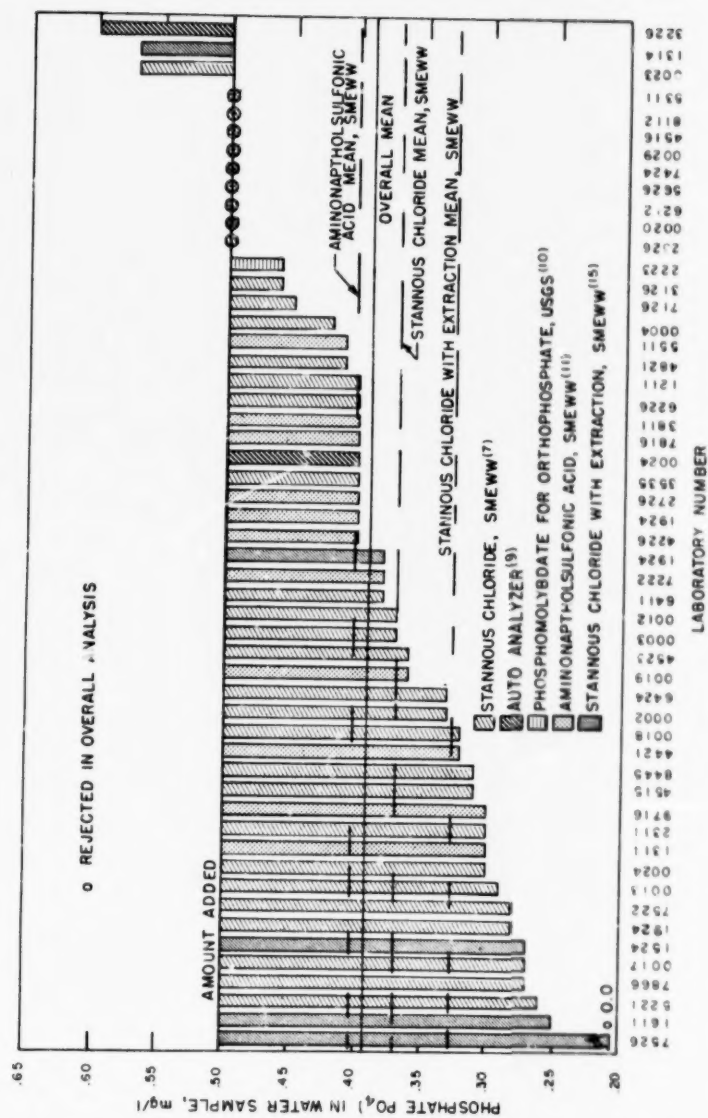


Figure 15. Bar graph for ortho phosphate in sample 3.

Any of the methods used should be adequate for routine use, but for measurement of very low concentrations, the stannous chloride method appears preferable.

NITRATE NITROGEN (Tables 8-10, Figures 16-21)

The nitrate procedures selected for study were the phenoldisulfonic acid method⁽²⁰⁾ and the brucine method⁽²⁴⁾ in the 12th edition of Standard Methods, and the modified brucine procedure of Jenkins and Medsker.⁽²⁵⁾ The chromotropic acid procedure of West and Ramachandran⁽²¹⁾ was submitted to several selected laboratories suggested by Dr. West.

Since chlorides are considered the greatest source of error in nitrate measurement, the three samples were designed to contain the same concentration of nitrate but varying concentrations of chloride.

The most widely used method was the phenoldisulfonic acid procedure in Standard Methods. This method not only produced the lowest results, but also the most widely scattered. In sample 3, containing 400 mg/liter chloride, the mean error seems to indicate that the phenoldisulfonic acid procedure was the best, but the standard deviation shows that the best precision was produced by the modified brucine and chromotropic acid methods. The bar graphs clearly illustrate the extreme variation in the phenoldisulfonic acid results and the much greater precision of all the other methods. The Standard Method brucine, Jenkins and Medsker modified brucine, autoanalyzer (reduction), (19, 22) chromotropic acid, and ultraviolet⁽²⁷⁾ procedures all appear capable of accurate nitrate measurement in samples containing up to 200 mg/liter chloride. Although all of these methods produced high results at a chloride concentration of 400 mg/liter, they were in good agreement with each other. Considering the entire study, the best precision and accuracy was obtained with the Jenkins and Medsker brucine method. The chromotropic acid method produced nearly the same precision and accuracy, but was used by only five participants. The small number of participants reduced the reliability of statistical evaluation. The polarograph,⁽²⁶⁾ used by only two participants, produced high and divergent results.

AMMONIA NITROGEN (Tables 11-13, Figure 22-27)

Nearly half the participants used distillation with nesslerization⁽³³⁾ for the ammonia measurement. Nearly a fourth used distillation with titration,⁽³⁴⁾ and the same number used direct nesslerization.⁽³⁵⁾ The direct nesslerization procedure produced the greatest accuracy and precision in all three samples. The results obtained for sample 1 (0.2 mg/liter) by all other methods except direct nesslerization were high.

Table 8. SUMMARY OF DATA ON NITRATE NITROGEN
Sample 1 (1.0 mg/liter added + 10 mg/liter Cl⁻)

Method	Outliers not included	Number of results included	Mean	Mean error	Standard deviation	95% tolerance limits	Relative standard deviation	Relative error
Phenoldisulfonic acid, SMEWW	1	46	0.62	-0.38	0.461	±1.10	74.4	38.0
Brucine, SMEWW	1	23	1.02	+0.02	0.289	±0.77	28.2	2.0
Brucine, Jenkins and Medsker	1	17	0.94	-0.06	0.053	±0.15	5.5	6.0
Autocatalyzer		8	1.09	+0.09	0.179	±0.67	16.4	9.0
Chromotropic Acid		5	0.97	-0.03	0.080	±0.40	8.1	3.0
Ultraviolet, SMEWW		4	1.00	0.00	0.103	±0.65	10.3	0.0
Polarograph, SMEWW		2	1.28	+0.28	0.233	-----	18.1	28.0
Phenoldisulfonic acid, USGS		1	0.00	-----	-----	-----	-----	-----
Reduction, Pappenbagen and Looker		1	1.02	-----	-----	-----	-----	-----
Brucine, Jenkins and Medsker (modified)		1	0.84	-----	-----	-----	-----	-----
2,6-Xylenol, Montgomery and Dymock		1	0.98	-----	-----	-----	-----	-----
Reduction, USGS		1	1.22	-----	-----	-----	-----	-----
Micro Method, Public Health Engineering Abstracts		1	0.10	-----	-----	-----	-----	-----
Steam Distillation, Bremner and Keeney		1	0.98	-----	-----	-----	-----	-----
Overall	3	112	0.83	-0.17	0.397	±0.89	47.6	17.0

Table 9. SUMMARY OF DATA ON NITRATE NITROGEN
Sample 2 (1.0 mg/liter added + 200 mg/liter Cl⁻)

Method	Outliers not included	Number of results included	Mean	Mean error	Standard deviation	95% tolerance limits	Relative standard deviation	Relative error
Phenoldisulfonic acid, SMEWW	1	46	0.69	-0.31	0.399	+0.95	57.9	31.0
Brucine, SMEWW	3	21	1.01	+0.01	0.140	±0.36	13.8	1.0
Brucine, Jenkins and Medsker	1	17	1.00	0.00	0.080	±0.22	7.9	0.0
Autoanalyzer		8	1.12	+0.12	0.186	±0.69	16.6	12.0
Chromotropic Acid	1	4	1.00	0.00	0.013	±0.08	1.2	0.0
Ultraviolet, SMEWW		4	1.06	+0.08	0.082	±0.52	7.5	8.0
Polarograph, SMEWW		2	1.44	+0.44	0.346	-----	24.1	44.0
Phenoldisulfonic acid, USGS	1	1	1.00	-----	-----	-----	-----	-----
Reduction, Pappenhiagen and Looker	1	1	0.92	-----	-----	-----	-----	-----
Brucine, Jenkins and Medsker (modified)		1	0.93	-----	-----	-----	-----	-----
2,6-Xylenol, Montgomery & Dymock		1	1.10	-----	-----	-----	-----	-----
Reduction, USGS		1	1.28	-----	-----	-----	-----	-----
Micro Method, Public Health Engineering Abstracts		1	0.50	-----	-----	-----	-----	-----
Steam Distillation, Bremner and Keeney		1	0.97	-----	-----	-----	-----	-----
Overall	4	111	0.89	-0.11	0.333	±0.73	37.5	11.0

Table 10. SUMMARY OF DATA ON NITRATE NITROGEN

Sample 3 (1.0 mg/liter added + 400 mg/liter Cl⁻)

Method	Outliers not included	Number of results included	Mean	Mean error	Standard deviation	95% tolerance limits	Relative standard deviation	Relative error
Phenoldisulfonic acid, SMEWW	1	45	0.81	-0.19	0.436	±1.05	53.8	19.0
Brucine, SMEWW	2	22	1.28	+0.28	0.217	±0.58	16.8	28.0
Brucine, Jenkins and Medsker	1	17	1.26	+0.26	0.117	±0.33	9.2	26.0
Autoanalyzer		8	1.42	+0.42	0.227	±0.84	15.9	42.0
Chromotropic acid		5	1.38	+0.38	0.128	±0.65	9.2	38.0
Ultraviolet, SMEWW		4	1.42	+0.42	0.03	±0.21	2.4	42.0
Polarograph, SMEWW		2	1.89	+0.89	0.446	-----	23.6	89.0
Phenoldisulfonic Acid, USGS		1	2.20	-----	-----	-----	-----	-----
Reduction, Pappenhagen and Looker		1	1.41	-----	-----	-----	-----	-----
Brucine, Jenkins and Medsker (modified)		1	1.22	-----	-----	-----	-----	-----
2, 6-Xylenol, Montgomery and Dymock		1	1.30	-----	-----	-----	-----	-----
Reduction, USGS		1	1.39	-----	-----	-----	-----	-----
Micro Method, Public Health Engineering Abstracts		1	0.15	-----	-----	-----	-----	-----
Steam Distillation, Brenner and Keeney		1	1.20	-----	-----	-----	-----	-----
Overall	4	110	1.12	+0.12	0.433	±0.95	38.7	12.0

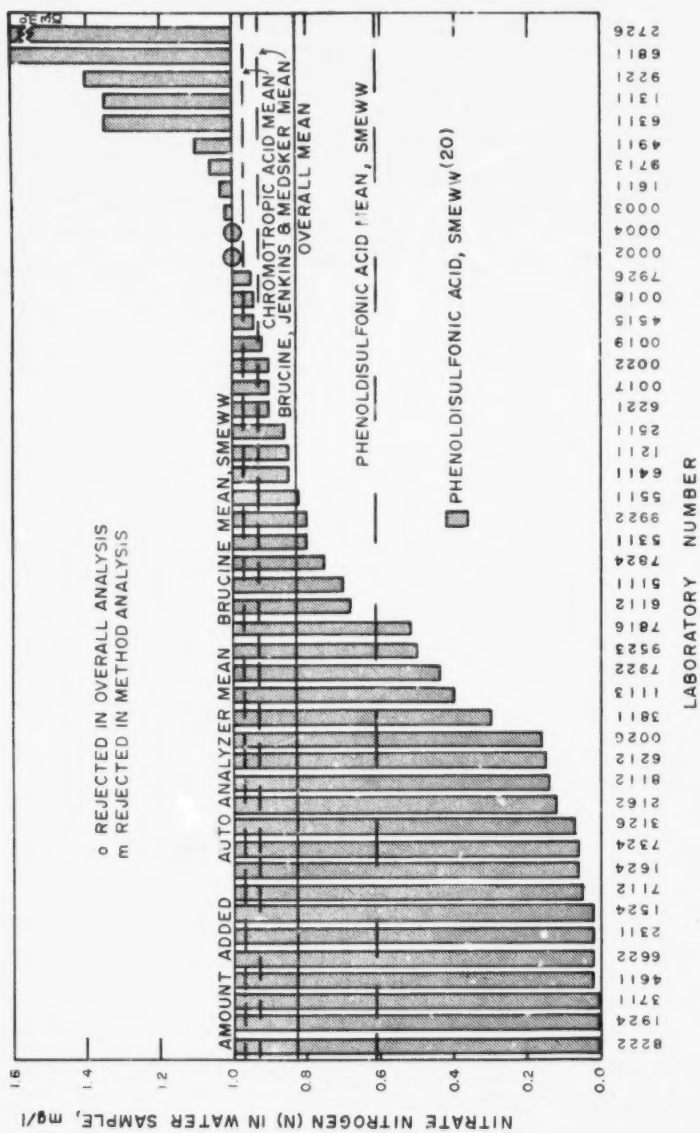


Figure 16. Bar graph for nitrate nitrogen in sample 1.

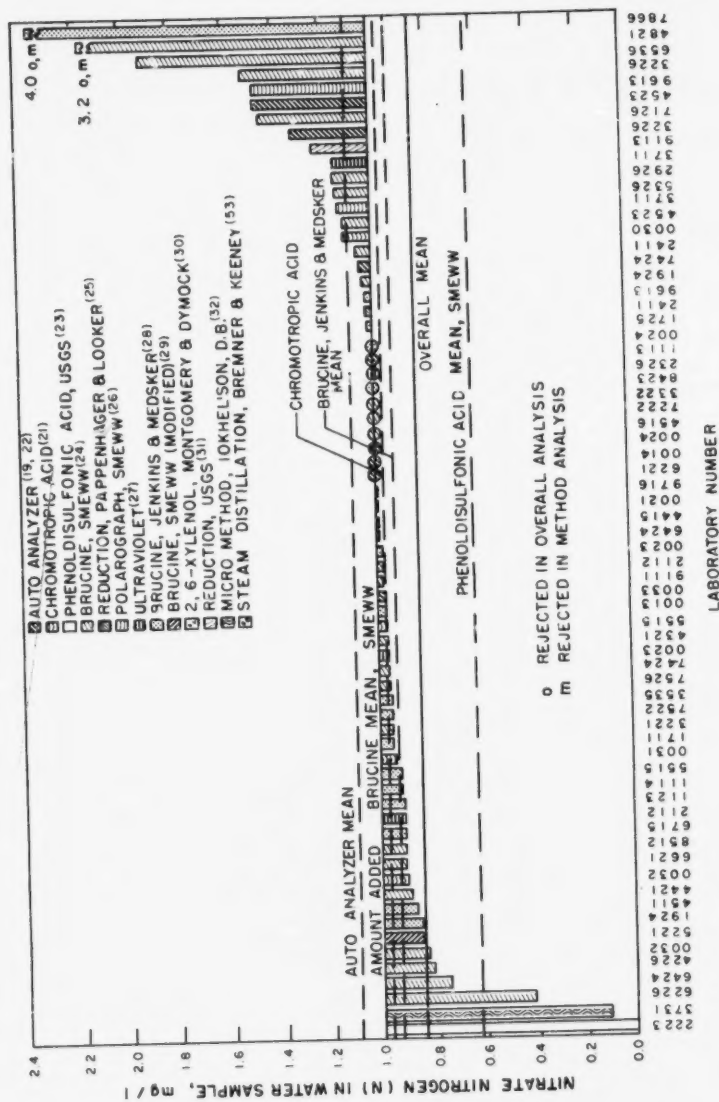


Figure 17. Bar graph for nitrate nitrogen in sample 1.

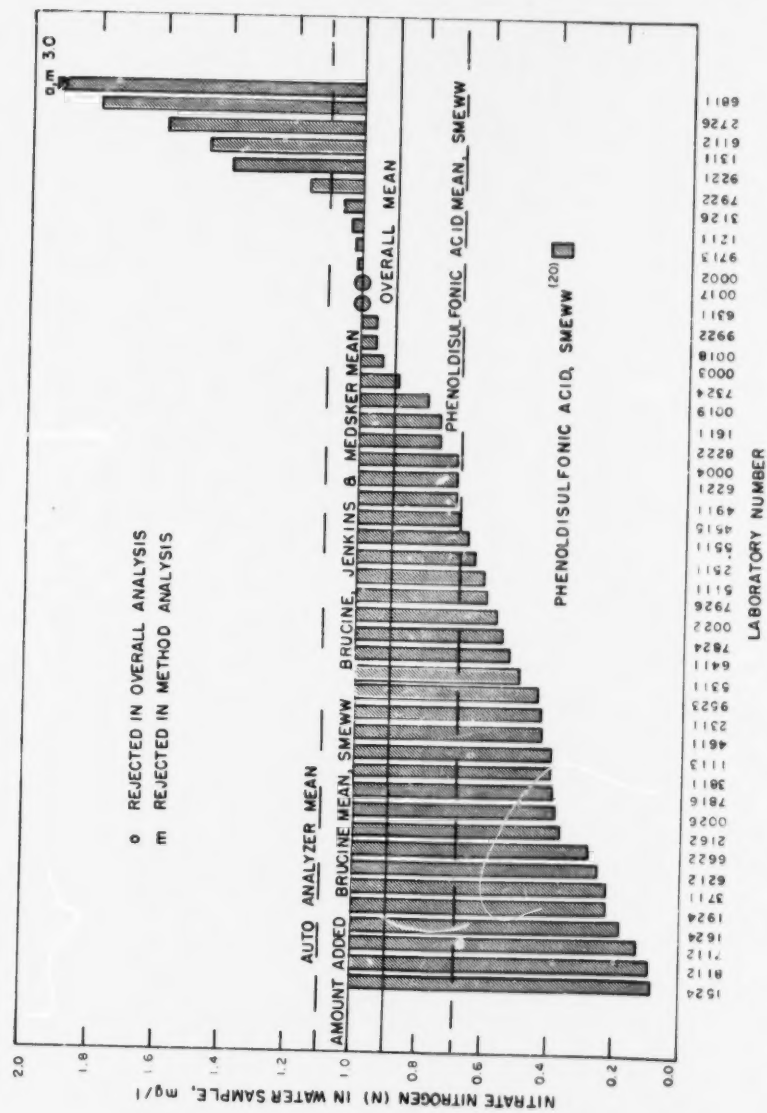


Figure 16. Bar graph for nitrate nitrogen in sample 2.

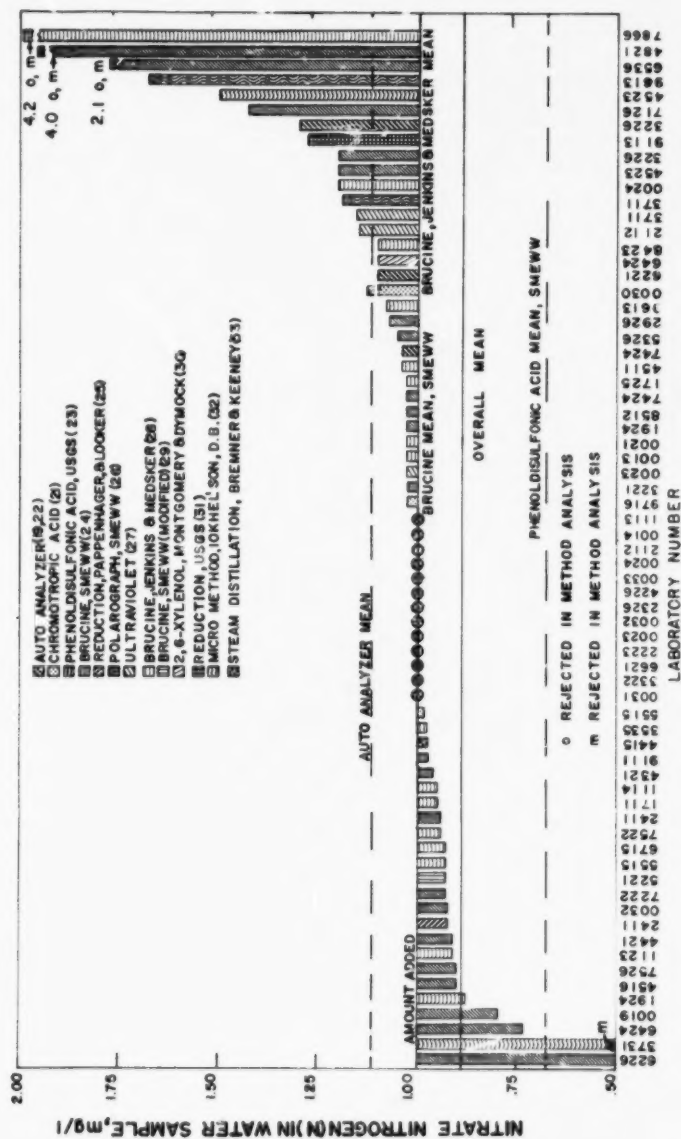


Figure 19. Bar graph for nitrate nitrogen in sample 2.

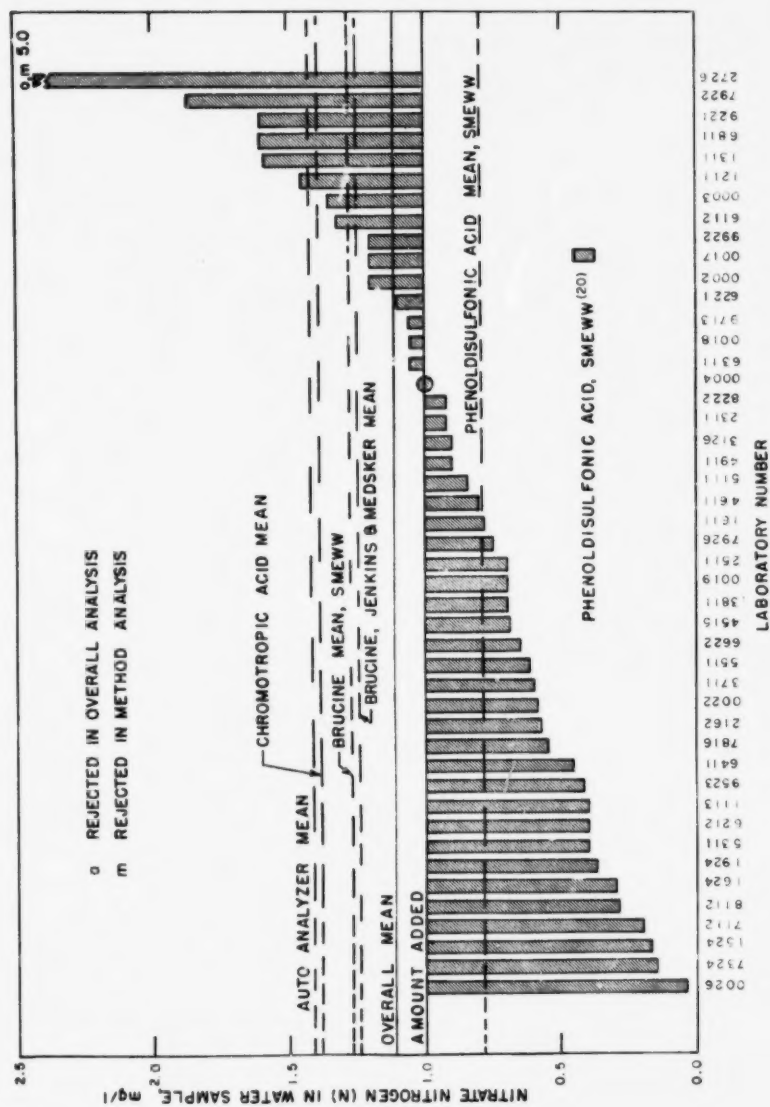


Figure 20. Bar graph for nitrate nitrogen in sample 3.

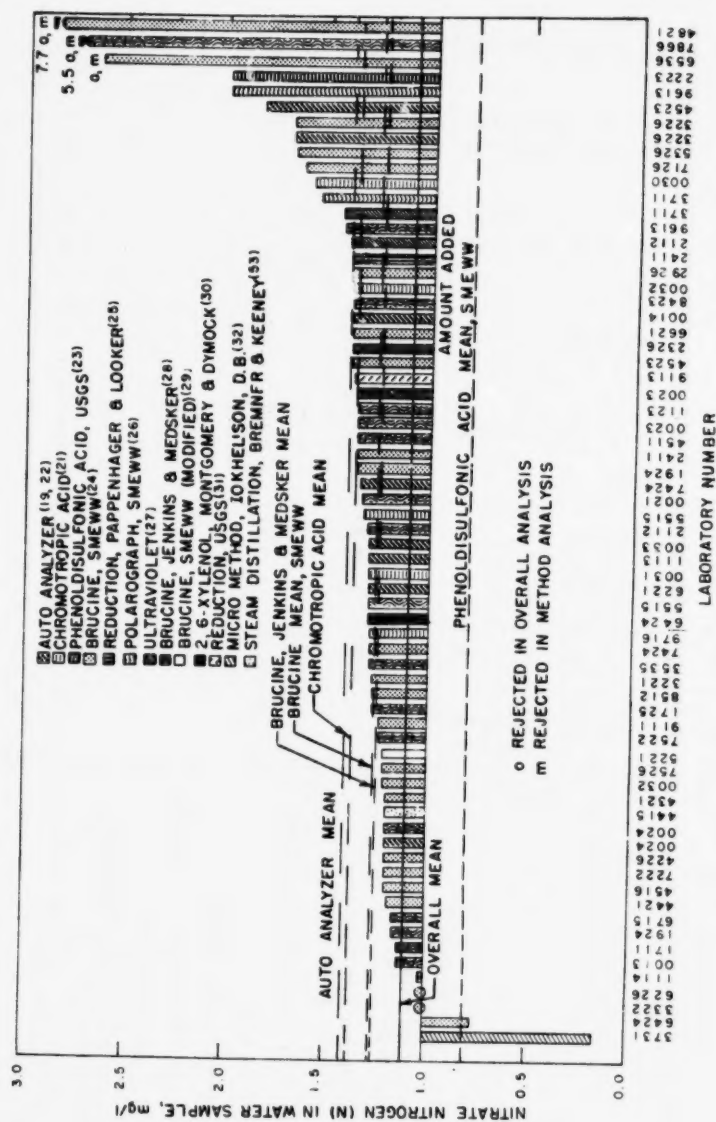


Figure 21. Bar graph for nitrate nitrogen in sample 3.

Table 11. SUMMARY OF DATA ON AMMONIA NITROGEN

Sample 1 (0.20 mg/liter added)

Method	Outliers not included	Number of results included	Mean	Mean error	Standard deviation	95% tolerance limits	Relative standard deviation	Relative error
Distillation with Nesslerization, SMEWW	1	44	0.22	+0.02	0.100	± 0.24	46.3	10.0
Distillation with Titration, SMEWW	1	21	0.24	+0.04	0.167	± 0.45	69.8	20.0
Direct Nesslerization, SMEWW	2	20	0.20	0.00	0.077	± 0.21	38.1	0.0
Autoanalyzer		7	0.28	+0.08	0.094	± 0.37	33.8	40.0
Nesslerization, USGS		1	0.36	-----	-----	-----	-----	-----
Indophenol, Rossum and Villaruz		1	0.22	-----	-----	-----	-----	-----
Riley and Sinhaseni		1	0.21	-----	-----	-----	-----	-----
Steam Distillation, Bremner and Keeney		1	0.50	-----	-----	-----	-----	-----
Overall	5	95	0.22	+0.02	0.106	± 0.23	47.9	10.0

Table 12. SUMMARY OF DATA ON AMMONIA NITROGEN

Sample 2 (0.80 mg/liter added)

Method	Outliers not included	Number of results included	Mean	Mean error	Standard deviation	95% tolerance limits	Relative standard deviation	Relative error
Distillation with Nesslerization, SMEWW	3	42	0.73	-0.07	0.155	± 0.37	21.2	8.7
Distillation with Titration, SMEWW	2	20	0.76	-0.04	0.218	± 0.55	28.6	5.0
Direct Nesslerization, SMEWW	2	20	0.80	0.00	0.090	± 0.24	11.2	0.0
Autoanalyzer		7	0.79	-0.1	0.084	± 0.33	10.6	1.2
Nesslerization, USGS		1	1.20	-----	-----	-----	-----	-----
Indophenol, Rossum and Villaruz		1	0.80	-----	-----	-----	-----	-----
Riley and Sirinhaseni		1	0.81	-----	-----	-----	-----	-----
Steam Distillation, Bremner and Keeney		1	0.91	-----	-----	-----	-----	-----
Overall	5	95	0.77	-0.03	0.176	± 0.39	22.8	3.7

Table 13. SUMMARY OF DATA ON AMMONIA NITROGEN

Sample 3 (1.50 mg/liter added)

Method	Outliers not included	Number of results included	Mean	Mean error	Standard deviation	95% tolerance limits	Relative standard deviation	Relative error
Distillation with Nesslerization, SMEWW	3	42	1.44	-0.06	0.261	± 0.63	18.0	4.0
L-stillation with Titration, SMEWW		21	1.46	-0.04	0.315	± 0.85	21.6	2.6
Direct Nesslerization, SMEWW	1	21	1.49	0.01	0.174	± 0.47	11.6	0.6
Autoanalyzer		7	1.46	-0.04	0.148	± 0.59	10.1	1.2
Nesslerization, USGS		1	1.80	-----	-----	-----	-----	-----
Indophenol, Rossum and Villaruz		1	1.50	-----	-----	-----	-----	-----
Riley and Sinhaseni		1	1.49	-----	-----	-----	-----	-----
Steam Distillation, Bremner and Keeney		1	0.39	-----	-----	-----	-----	-----
Overall	4	95	1.47	-0.03	0.258	± 0.57	17.5	2.0

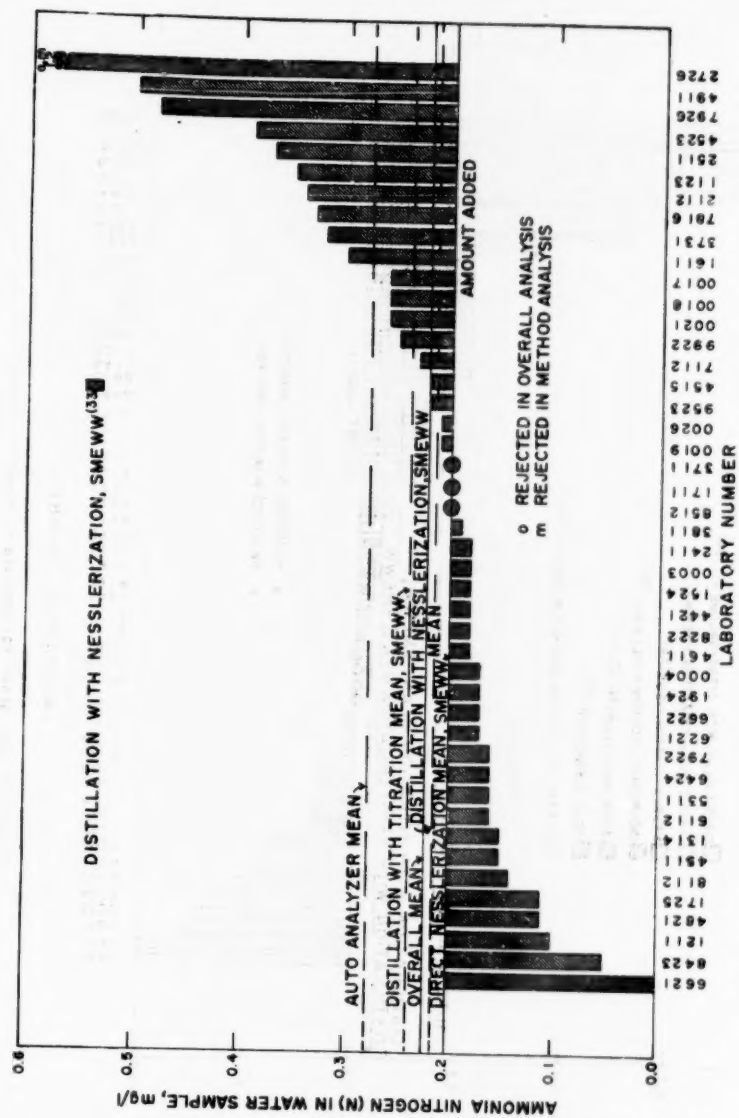


Figure 22. Bar graph for ammonia nitrogen in sample 1.

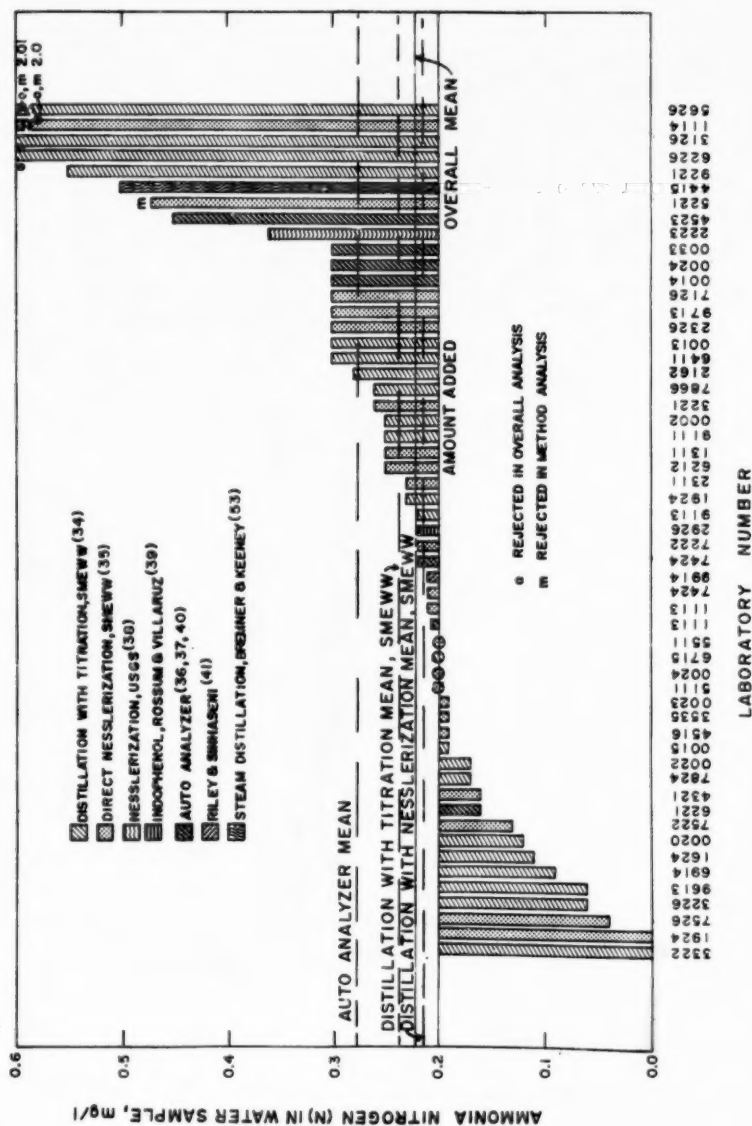


Figure 23. Bar graph for ammonia nitrogen in sample 1.

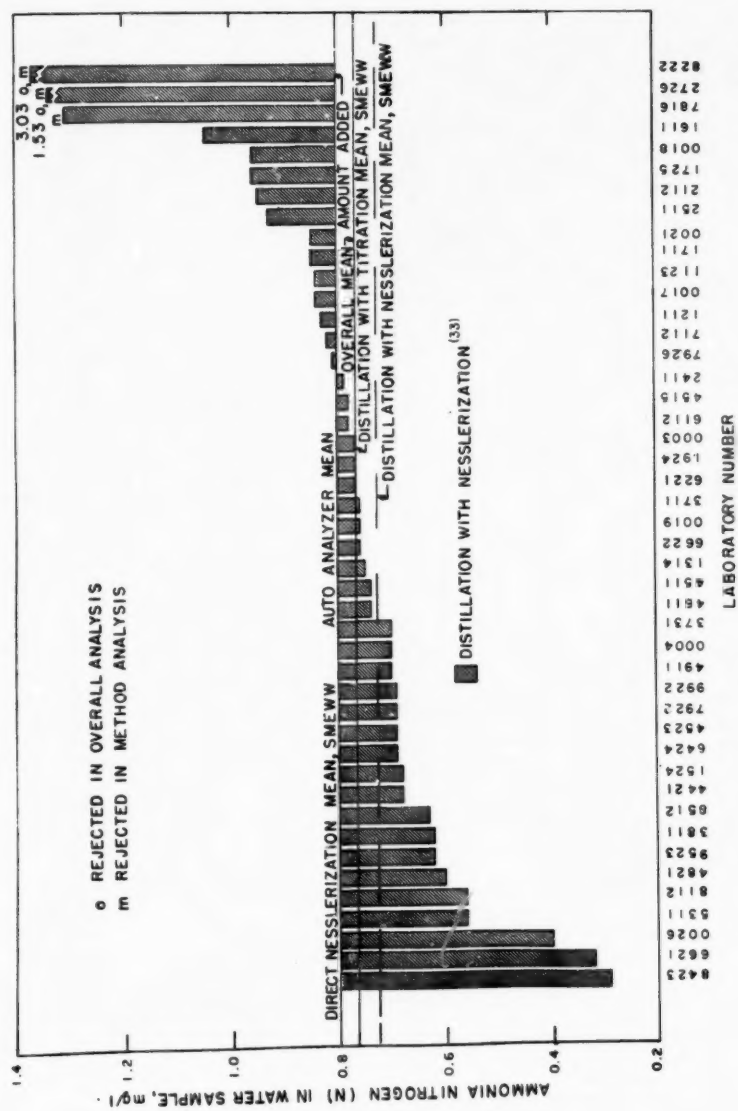


Figure 24. Bar graph for ammonia nitrogen in sample 2.

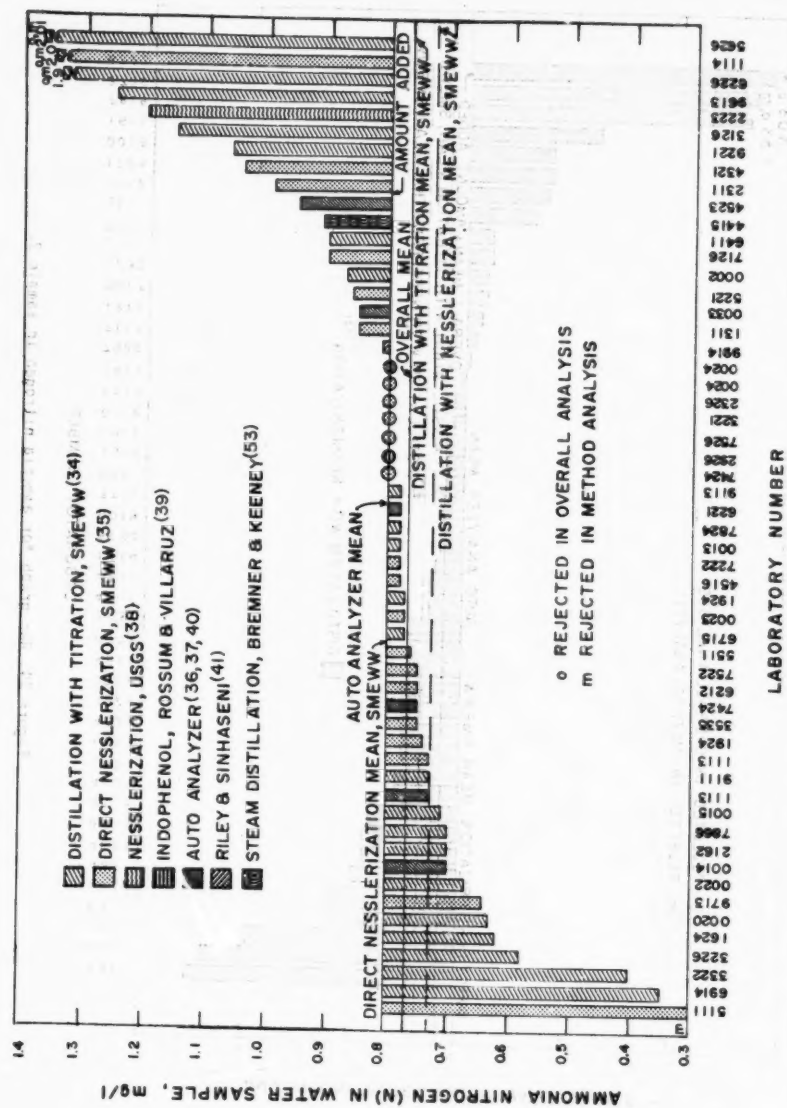


Figure 25. Bar graph for ammonia nitrogen in sample 2.

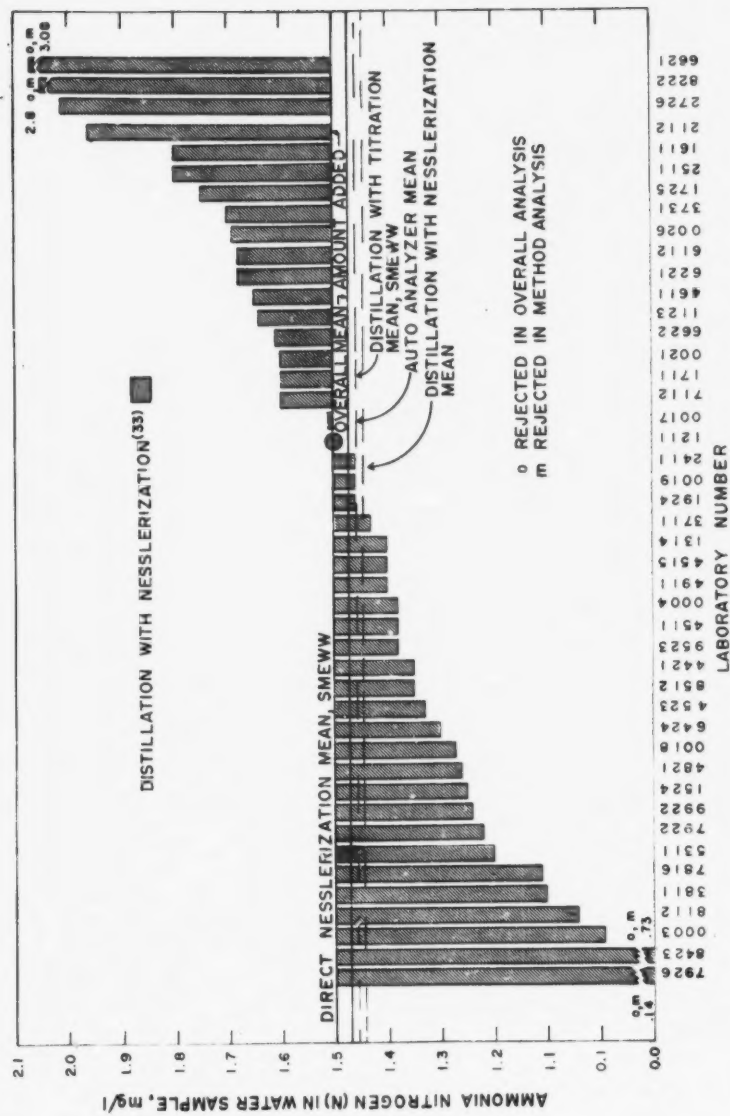


Figure 2B. Bar graph for ammonia nitrogen in sample 3.



Figure 27. Bar graph for ammonia nitrogen in sample 3.

The results for sample 2 (0.8 mg/liter) and 3 (1.5 mg/liter) were low when distillation was used, and also were less precise. Results with the autoanalyzer (36, 37, 40) were high on sample 1, but agreed closely with the direct nesslerization results on samples 2 and 3.

A procedure by Riley and Sinhaseni⁽⁴¹⁾ and an indophenol method by Rossum and Villaruz⁽³⁹⁾ were each used by one participant, and both produced excellent results for all three samples.

Since no interferences were present in any of the samples, it is logical that direct nesslerization should produce the best accuracy and precision because of the minimum of manipulative steps.

The relative standard deviation indicates similar precision for samples 2 and 3, considering all methods. For sample 1, however, the relative standard deviation, which more than doubled for the distilled samples and more than tripled for the undistilled samples, indicated that concentrations of 0.20 mg/liter are difficult to determine with precision.

ORGANIC NITROGEN (Tables 14-16, Figures 28-33)

The majority of participants used the technique of boiling off ammonia, followed by kjeldahl digestion and titration.⁽⁴³⁾ Nearly as many used the same technique except for the substitution of nesslerization instead of titration.⁽⁴²⁾ A large number determined total kjeldahl nitrogen and subtracted ammonia nitrogen, after measuring both by nesslerization.⁽⁴⁴⁾

From the data, it is difficult to arrive at any conclusions other than the obvious one that few analysts measure organic nitrogen accurately, regardless of method used. It appears that boiling off ammonia, following with a kjeldahl digestion and measurement by nesslerization may produce slightly better accuracy and precision than the other techniques, but the difference in results is not statistically significant.

Regardless of method, the precision as shown by the relative standard deviation is similar for samples 1 and 2, but becomes much worse for sample 3, which contained only 0.20 mg/liter. Accuracy decreases with lower concentrations as shown by the progressive rise in the relative error. Apparently a concentration of 0.20 mg/liter cannot be measured with acceptable accuracy and precision, even when no interferences are present in the sample.

Table 14. SUMMARY OF DATA ON ORGANIC NITROGEN

Sample 1 (1.5 mg/liter added)

Method	Outliers not included	Number of results included	Mean	Mean error	Standard deviation	95% tolerance limits	Relative standard deviation	Relative error
Boiled, Kjeldahl and Titration, SMEWW	2	30	1.16	-0.34	0.633	±1.61	54.7	22.6
Boiled, Kjeldahl and Nesslerization, SMEWW	1	26	1.36	-0.14	0.586	±1.52	43.1	9.3
Kjeldahl minus ammonia by nesslerization, SMEWW	1	16	1.44	-0.06	0.660	±1.91	45.9	4.0
Autoanalyzer		3	1.82	+0.32	0.766	-----	42.1	21.3
Kjeldahl minus ammonia by titration, SMEWW		1	1.32	-----	-----	-----	-----	-----
Kabat and Mayer		1	1.40	-----	-----	-----	-----	-----
Organic nitrogen, nesslerization, SMEWW, 10th ed.		1	0.36	-----	-----	-----	-----	-----
Boiled, Kjeldahl and Nesslerization, SMEWW, modified		1	2.00	-----	-----	-----	-----	-----
Kjeldahl, USGS		1	1.40	-----	-----	-----	-----	-----
Kjeldahl, indophenol, Possum and Villaruz		1	1.40	-----	-----	-----	-----	-----
Nitrogen (albuminoid), SMEWW		1	1.06	-----	-----	-----	-----	-----
Total Nitrogen, Bremner		1	1.26	-----	-----	-----	-----	-----
Overall	3	84	1.33	-0.17	0.644	±1.45	48.3	11.3

Table 15. SUMMARY OF DATA ON ORGANIC NITROGEN

Sample 2 (0.8 mg/liter added)

Method	Outliers not included	Number of results included	Mean	Mean error	Standard deviation	95% tolerance limits	Relative standard deviation	Relative error
Boiled, Kjeldahl and Titration, SMEWW	1	31	0.83	+0.03	0.373	±0.94	44.8	3.7
Boiled, Kjeldahl and Nesslerization, SMEWW	1	26	0.70	-0.10	0.364	±0.85	52.1	12.5
Kjeldahl minus ammonia by nesslerization, SMEWW	1	16	0.87	+0.07	0.458	±1.32	52.6	8.6
Autoanalyzer		3	0.69	-0.11	0.101	±0.99	14.6	13.7
Kjeldahl minus ammonia by titration, SMEWW		1	0.65	-----	-----	-----	-----	-----
Kabat and Mayer		1	0.80	-----	-----	-----	-----	-----
Organic nitrogen, nesslerization, SMEWW, 10th ed.		1	0.16	-----	-----	-----	-----	-----
Boiled, Kjeldahl and nesslerization, SMEWW, modified		1	1.67	-----	-----	-----	-----	-----
Kjeldahl, USGS		1	0.67	-----	-----	-----	-----	-----
Kjeldahl, indophenol, Possum and Villaruz		1	0.83	-----	-----	-----	-----	-----
Nitrogen (albuminoid) SMEWW		1	0.54	-----	-----	-----	-----	-----
Total Nitrogen, Bremner		1	0.67	-----	-----	-----	-----	-----
Overall	3	84	0.79	-0.01	0.386	±0.87	49.1	1.2

Table 16. SUMMARY OF DATA ON ORGANIC NITROGEN

Sample 3 (0.2 mg/l added)

Method	Outliers not included	Number of results included	Mean	Mean error	Standard deviation	95% tolerance limits	Relative standard deviation	Relative error
Boiled, Kjeldahl and Titration, SMEWW	2	29	0.34	+0.14	0.360	----- ^a	104.4	70.0
Boiled, Kjeldahl and Nesslerization, SMEWW	1	26	0.31	+0.11	0.290	±0.75	94.8	55.0
Kjeldahl minus ammonia by nesslerization, SMEWW	1	15	0.34	+0.14	0.235	±0.69	68.8	70.0
Autoanalyzer		3	0.49	+0.29	0.406	±4.02	82.2	145.0
Kjeldahl minus ammonia by titration, SMEWW	1	1	0.45	-----	-----	-----	-----	-----
Kabat and Mayer		1	0.40	-----	-----	-----	-----	-----
Organic nitrogen, nesslerization, SMEWW, 10th ed.		1	0.02	-----	-----	-----	-----	-----
Boiled, Kjeldahl and nesslerization, SMEWW, modified		1	1.40	-----	-----	-----	-----	-----
Kjeldahl, USGS		1	0.10	-----	-----	-----	-----	-----
Kjeldahl, indophenol, Possum and Villaruz		1	0.20	-----	-----	-----	-----	-----
Nitrogen (albuminoid) SMEWW		1	0.10	-----	-----	-----	-----	-----
Total Nitrogen, Bremner		1	2.49	-----	-----	-----	-----	-----
Overall	8	77	0.30	+0.10	0.26	±0.39	86.6	50.0

^a Nonnormal distribution, no value calculated.

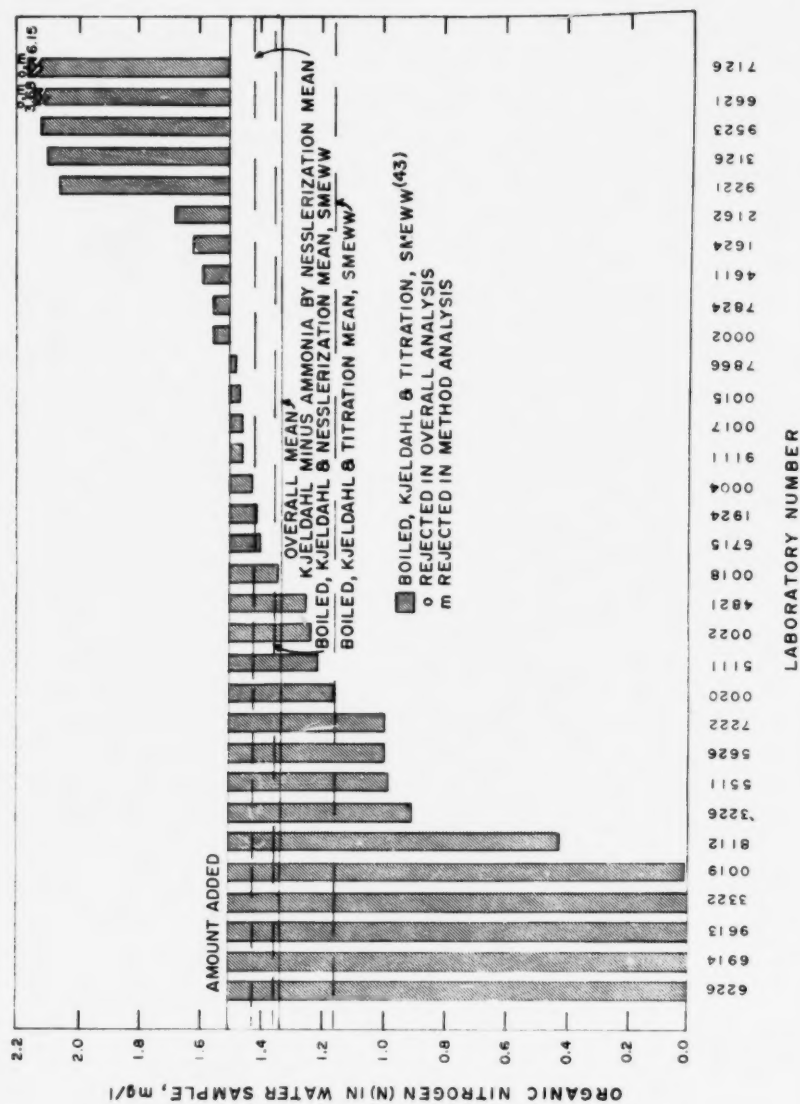


Figure 28. Bar graph for organic nitrogen in sample 1.



Figure 20. Bar graph for organic nitrogen in sample 1.

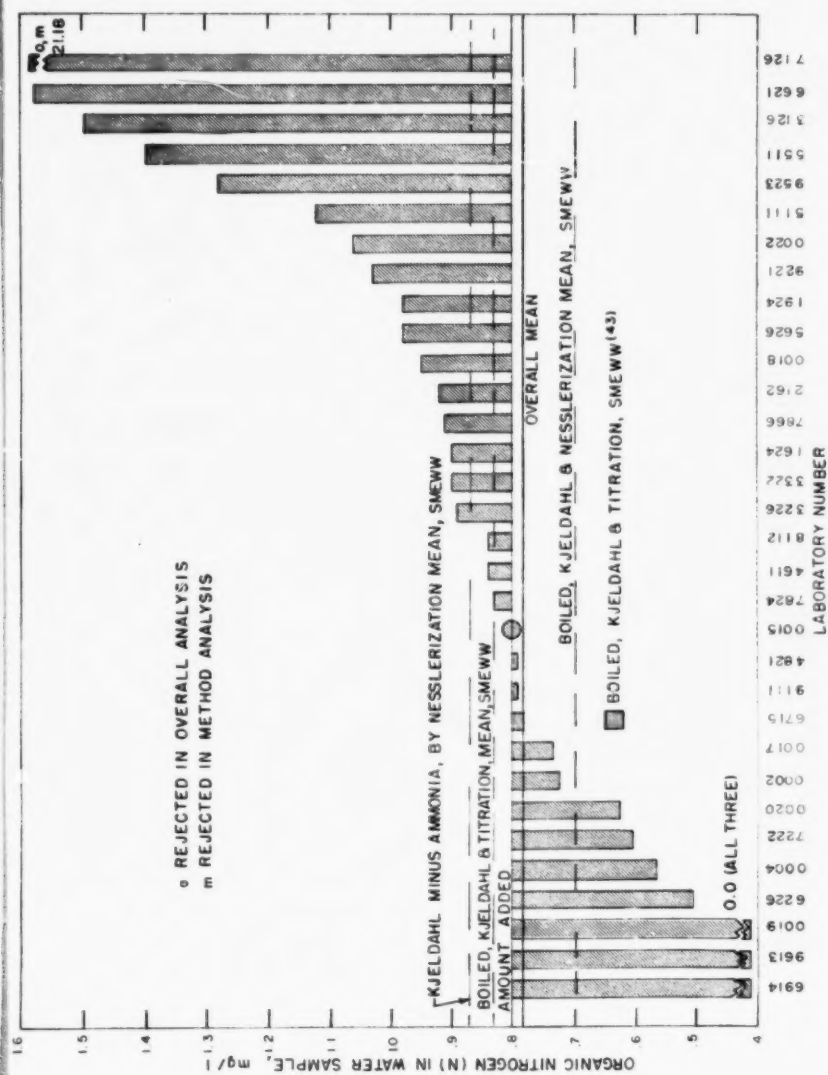


Figure 30. Bar graph for organic nitrogen in sample 2.

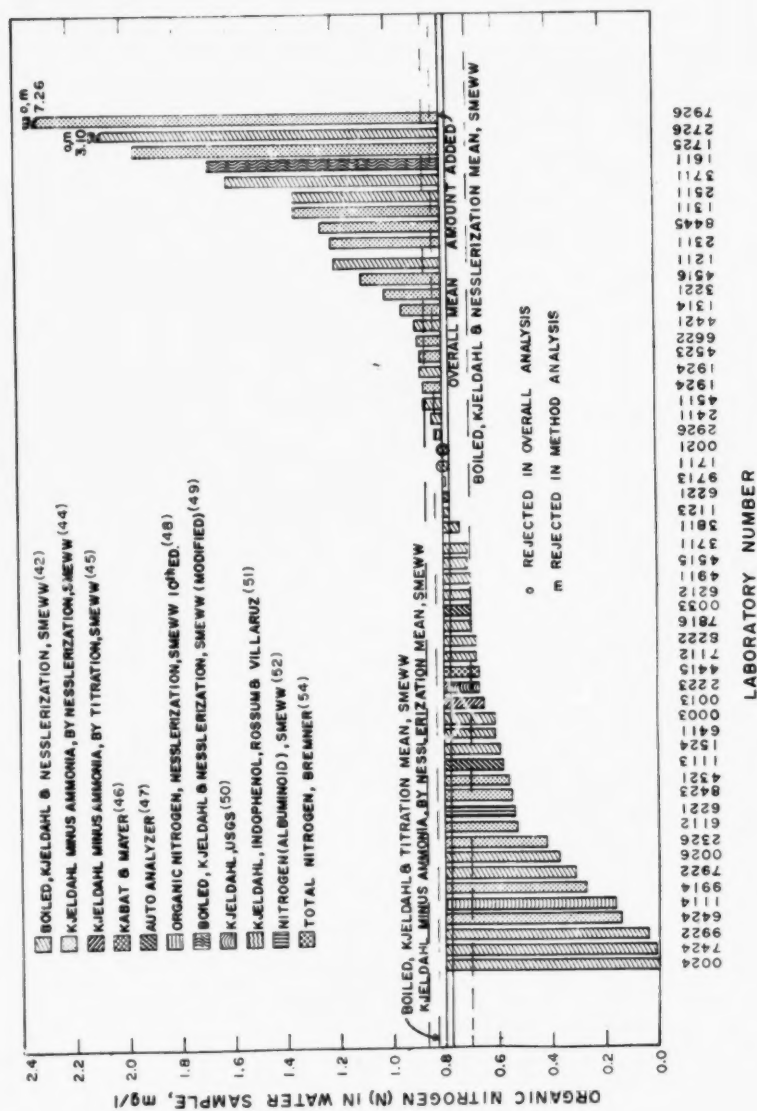


Figure 31. Bar graph for organic nitrogen in sample 2.

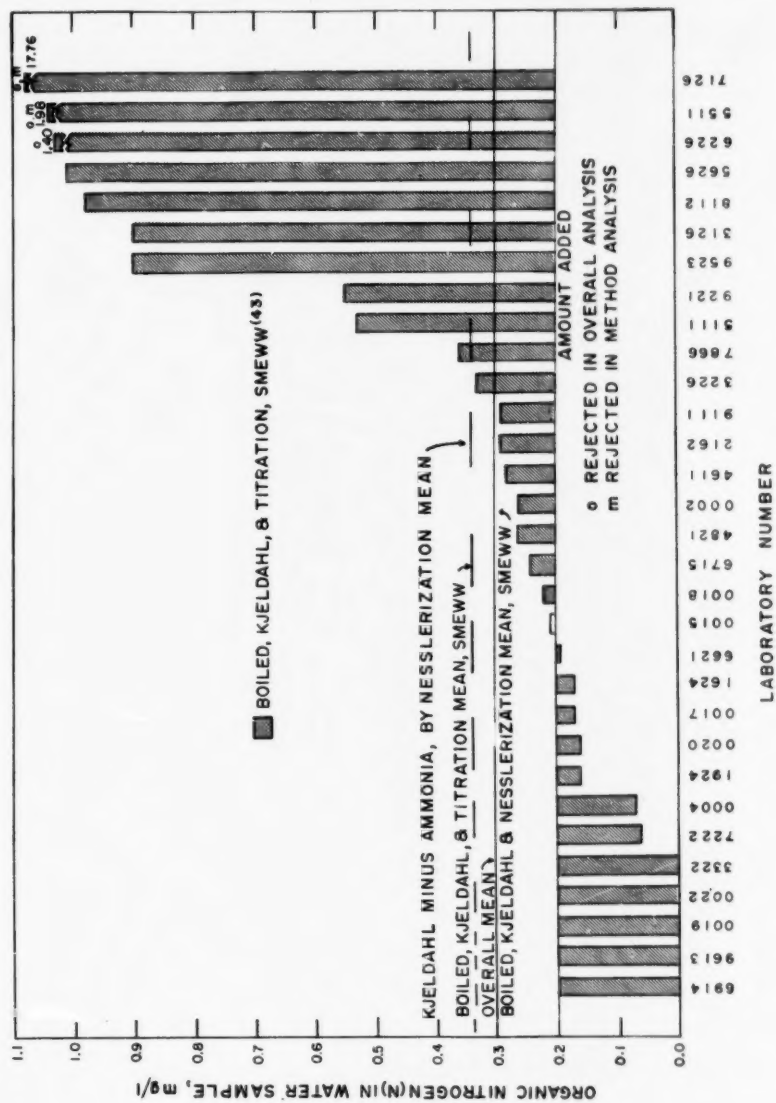


Figure 32. Bar graph for organic nitrogen in sample 3.

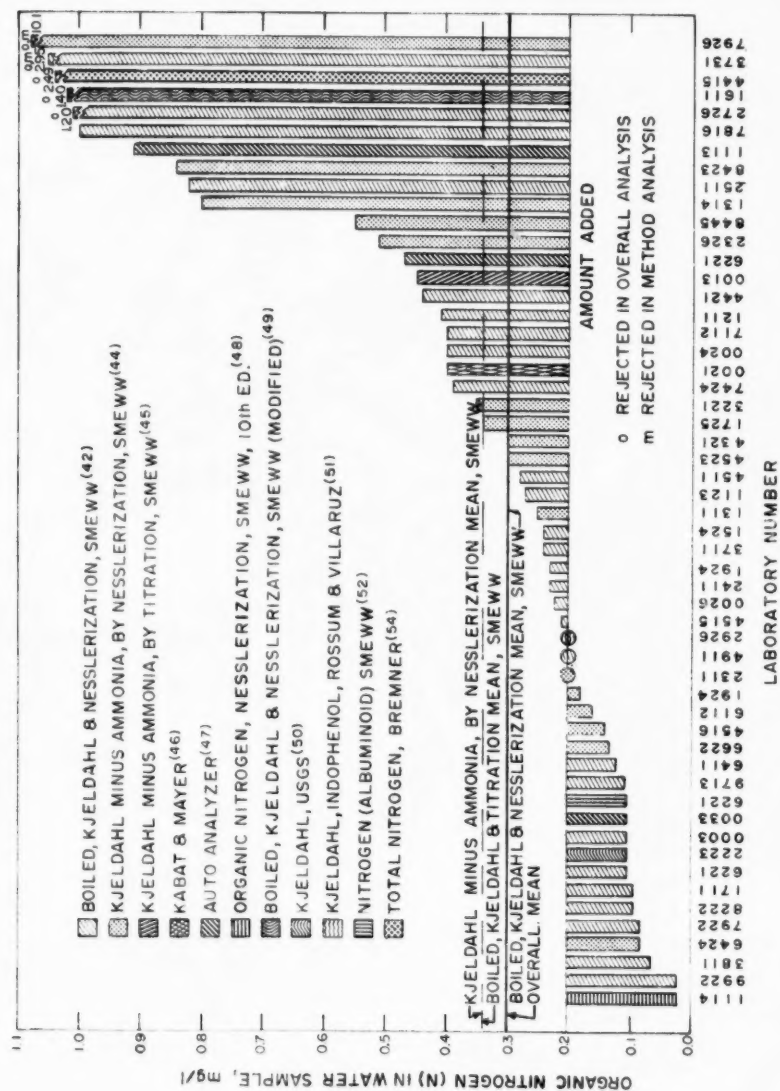


Figure 33. Bar graph for organic nitrogen in sample 3.

COMMENTS OF THE PARTICIPANTS

The following comments were received from individual participants.

Silica

A slight advantage of the Morrison and Wilson silica method over the method in the 12th edition of Standard Methods is the combined acid-molybdate reagent, which is stable.

Standards should be run with each determination, since they seemed to vary from day to day.

Phosphate

In the aminonaphtholsulfonic acid procedure, full color does not develop until 10 minutes, rather than 5 minutes as indicated in Standard Methods. Fresh aminonaphtholsulfonic acid should be used for best results.

In the aminonaphtholsulfonic acid procedure, we verified that the samples should be read after exactly 5 minutes, since several minutes delay seemed to change the result several percent.

Phosphates were filtered through a membrane filter, which is not listed in Standard Methods.

Nitrate Nitrogen

The phenoldisulfonic acid procedure is long and tedious. Spattering of sample is a significant source of error.

The brucine tests for nitrate may have some merit in providing correct results, but, in general, are sloppy to perform. Normally, we do not find the brucine method to compare as favorably as the alkaline ferrous sulfate - silver sulfate reduction method for the determination of nitrates when replicate samples are used.

The values obtained by the brucine method are a few percent lower than by the chromotropic acid method. In the brucine method, part of the nitrate reduces the intensity of the blank color. The lower absorbance obtainable for the blank was 0.030 for a 1-cm light path. Because of nonreproducibility and bias, standards must be run under identical conditions along with samples.

The phenoldisulfonic acid method gave low results, even after chloride removal. The reproducibility is bad and occasional loss of nitrate on evaporation is observed, even with proper pH adjustment. The chromotropic acid method was also applied to the samples after removal of chloride as silver chloride using silver sulfate. The agreement is very good with results obtained with chloride present. A small correction of silver sulfate blank due to presence of traces of nitrate is necessary.

In chloride removal for nitrate analysis by the phenoldisulfonic acid method, some nitrate was lost during the AgCl precipitation.

The chromotropic acid procedure by West is entirely too tedious to work with and the 2.5-ml volume of sample is difficult to pipet accurately. It may be a more precise and/or specific method, but requires a great deal of manual dexterity of the analyst.

Results on repeated analyses could not be duplicated when determining nitrate by phenoldisulfonic acid. Chlorides were carefully removed, and ammonia was used as the alkali.

Chloride removal is important in the phenoldisulfonic acid procedure.

Evaluations of nitrate-nitrogen with the brucine method had to be made on the lower end of the calibration curve where some variable color development was observed when working with known standards. The accuracy of the reported values is questioned when only one analysis can be made at a specified dilution.

It is difficult to get completely nitrogen-free water for blanks.

For acceptable chloride precipitation in the phenoldisulfonic acid method for nitrate, it seemed almost a necessity to let the sample sit overnight in the dark.

The modified brucine procedure gave rather poor reproduction of a standard curve. Brucine is sensitive at concentrations below 0.2 mg/liter. Phenoldisulfonic acid will follow a reproducible straight line from 0-4 mg/liter and a useful curve to 6 mg/liter at 410 $m\mu$ on an "amplified" scale instrument such as the Beckman Model B. The brucine color is not stable overnight, but seems to be stable 20 to 30 minutes after heating. The modified brucine method is more rapid than the phenoldisulfonic acid method.

General

Sealed ampoules are an excellent method of transporting samples.

Participants should be requested to do more than a single analysis for each element in each sample, especially if the method is new to the analyst.

CONCLUSIONS

The determination of silica as described in Standard Methods should be changed to require the bicarbonate digestion, instead of merely including it as an optional step. The analyst also should be cautioned against allowing much of the sample to evaporate. Both the molybdosilicate and heteropoly blue methods are capable of acceptable accuracy and precision at the higher concentrations (15 to 30 mg/liter) but the molybdosilicate is the more widely used and precise method at the lower concentrations (5 mg/liter).

In analyzing for phosphate, the analyst must know which form of phosphate he is to measure and use the appropriate procedure. The stannous chloride method is the most widely used and produces acceptable accuracy and precision. The autoanalyzer appears to give satisfactory results down to 0.5 mg/liter, where accuracy and precision decrease.

The most widely used method for nitrate analysis is the phenol-sulfonic acid procedure, which, unfortunately, also appears to be the poorest. The results by this method were low for all three samples, and the greater accuracy and precision of all the other methods would make any of them a better choice. The Jenkins and Medsker brucine procedure produced the best overall results; and the chromotropic acid procedure, although used by fewer participants, appears to be similar in performance. The autoanalyzer produced acceptable accuracy and precision except in the presence of 400 mg/liter chloride, where all methods showed an apparent increase in nitrate content. Apparently, this much chloride still presents a problem.

The determination of ammonia by direct nesslerization produced the best accuracy and precision. Substantial error was introduced by distillation. This error might be overcome by distilling known standards to determine recovery efficiency. The autoanalyzer produced acceptable accuracy and precision except for sample 1. At the concentration of 0.20 mg/liter all methods showed reduced precision and accuracy.

Nesslerization and titration are equally popular for measuring organic nitrogen after boiling off the ammonia from the sample and kjeldahl digestion. Regardless of the method used, the precision and accuracy of the results are very poor for samples of high concentration

(0.8 to 1.5 mg/liter) and become unacceptable at a concentration of 0.2 mg/liter. The autoanalyzer performed poorly and inconsistently on this determination.

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APPENDICES

APPENDIX A.

TESTS FOR NORMALITY AND REJECTION OF OUTLIERS

Test for normality

The Kolmogorov-Smirnov goodness of fit test is used to determine whether the observations reported can reasonably be thought to have come from a normal distribution.*

Briefly, the test involves computing the observed cumulative frequency distribution (the percent of values less than or equal to each value in the distribution) and comparing it to the theoretical normal cumulative frequency distribution. The point at which the two distributions, theoretical and observed, show greatest divergence is determined. Reference of the value of the divergence to a table of critical values for the Kolmogorov-Smirnov goodness of fit test indicates whether such a large divergence is likely on the basis of chance. If such a large divergence is not likely, the distribution is designated as nonnormal; otherwise the distribution is designated as normal.

Tests for rejection of outliers

1. If the distribution is designated as nonnormal, the suspected outlier (the farthest value from the mean) is rejected only if the distance between it and the mean is greater than three standard deviations, otherwise the suspected outlier is accepted.

2. If the distribution is designated as normal and the sample size is less than or equal to 30, the suspected outlier, the farthest value from the mean, is tested for rejection by a method developed by Dixon.** Briefly, the test involves computing a ratio that compares the distance of the suspected value from its neighbors to the range of all or most all of the observations (depending on the exact number in the distribution). Reference of the ratio to a table of critical values for test ratios for gross errors indicates whether such a large ratio is likely on the basis of chance. If the ratio is greater than or equal to the critical value, the probability is small that the suspected outlier is from the sample distribution; hence, the outlier is rejected. If the ratio is less than the critical

* S. Siegel. *Nonparametric Statistics for the Behavioral Sciences*. McGraw-Hill Book Company, Inc. New York, N.Y. 1956. pp. 47-51.

** W.J. Dixon and F.J. Massey, Jr. *Introduction to Statistical Analysis*, Second edition. McGraw-Hill Book Company, Inc., New York, N.Y. 1957. p. 276.

value, it is not unlikely that the suspected outlier came from the sample distribution; hence, the suspected outlier is accepted.

3. If the distribution is designated as normal and the sample size is greater than 30, the suspected outlier is tested for rejection by a method developed by Santner.[†] This method employs the following statistic $\frac{\bar{X} - X_0}{s}$, where $\bar{X}$ is the sample mean, X_0 is the suspected outlier, the farthest value from the mean, and s is the sample standard deviation. This statistic is compared to a table of critical values to determine whether its value is larger than would be expected on the basis of chance. If the statistic is greater than or equal to the critical value, the suspected outlier is rejected; otherwise, the suspected outlier is accepted.

Application of test for normality and tests for rejection of outliers to ARS studies

The test for normality and subsequent test for rejection of outliers are applied to the observed data in two ways; first, to each method for a given substance at a given level of concentration, and then to a given substance at a given level of concentration regardless of method. In either case, it is first necessary to determine whether the original distribution is normal or nonnormal. If the original distribution is designated as nonnormal, method 1 is used in order to test the suspected outlier farthest from the mean for rejection. If the suspected outlier is not rejected, no further tests for normality or rejection of outliers are made and the distribution is designated as nonnormal. On the other hand, if the suspected outlier is rejected, the new distribution, which excludes the rejected observation, is then tested for normality. If the new distribution is nonnormal, the next suspected outlier is tested for rejection by method 1; and this cycle of testing for normality and testing for rejection of outliers continues until a suspected value is not rejected or the test for normality designates the distribution as normal. If the distribution is designated as normal, subsequent tests for rejection of outliers made by method 2 or 3 are the same as if the original distribution had been normal. This case is discussed next.

If the original distribution is designated as normal, or a new distribution that was originally nonnormal is designated as normal after the rejection of 1 or more outliers, and if the number of observations is not greater than 30, then method 2 is used in order to test the suspected outlier farthest from the mean for rejection. If the suspected outlier is not rejected, no further tests are made and the distribution is designated as normal. If the suspected outlier is rejected, then the suspected

[†] J. Santner. Personal communication

outlier farthest from the mean of the new distribution is tested for rejection and so on until the suspected value of a new distribution is not rejected, at which time no further tests are made and the final distribution is designated as normal. On the other hand, if the number of observations in the original distribution is greater than 30, method 3 is used to test the suspected outlier for rejection. If the suspected outlier is not rejected, no further tests are made and the distribution is designated as normal. If the suspected outlier is rejected, then the suspected outlier farthest from the mean of the new distribution, which excludes the rejected value, is tested for rejection. Testing for outliers continues by this method until a suspected outlier is not rejected or the number of observations is no longer greater than 30, in which case method 2 is used for testing for rejection of any remaining suspected outliers.

APPENDIX B.

GLOSSARY OF STATISTICAL TERMS

A glossary of statistical terms defined as they are used in this report is presented to ensure uniform and complete understanding.

Arithmetic mean	The sum of a series of test results divided by the number of tests in the series.
Median	Halfway point in the readings when they have been arranged in order of size (the middle reading of an odd number of readings, or the average of the middle two for an even number).
Accuracy	The correctness of a measurement, or the degree of correspondence between the results and the true value (actual amount added).
Accuracy data	Measurements that relate to the difference between the average test results and the true value when the latter is known or assumed. The following measures apply: <u>Average deviation from true value</u> - Average difference (when always considered as positive) between the mean determination for each laboratory and the true value. <u>Average percent deviation from true value</u> - Average of the differences between a laboratory's replicate results and the true value expressed as percentages of the true value. <u>Mean error</u> - The average difference with regard to sign of the test results from the true results. Also equal to the difference between the average of a series of test results and true results. <u>Relative error</u> - The absolute value of the mean error of a series of test results as a percentage of the true result.
Precision	A measure of the reproducibility of measurements, or the degree to which the measurements correspond to one another.

Precision data

Measurements that relate to the variation among the test results themselves, i.e., the scatter or dispersion of a series of test results without assumption of any prior information. The following measures apply:

Variance - Sum of squares of deviations of the average test results from the mean of the series divided by one less than the total number of average test results.

Standard deviation - Square root of the variance.

Relative standard deviation (coefficient of variation) - Standard deviation expressed as a percentage of the mean of a series of laboratory results.

Range - Difference in magnitude between the highest and lowest laboratory mean.

Average percent deviation within laboratory - Average of the differences between the replicate results from a laboratory and the mean of their results, expressed as percentage of their mean.

Confidence limits - Limits within which the true mean of the population (the theoretically infinite number of possible replications of the analysis) will lie with a given probability.

95% Tolerance limits - Limits within which one can state with chosen confidence that 95% of the individuals of a population will lie.

APPENDIX C.

ANALYTICAL REFERENCE SERVICE MEMBERSHIP

STATE AGENCIES

Alabama State Department of Public Health, Montgomery
Alabama Water Improvement Commission, Montgomery
Arizona State Department of Public Health, Phoenix
Arkansas State Department of Health, Little Rock
California Department of Water Resources, Los Angeles
California Department of Water Resources, Sacramento
California State Department of Public Health, Los Angeles
California State Department of Public Health, Air and Industrial Hygiene
Laboratory, Berkeley
California State Department of Public Health, Sanitation and Radiation
Laboratory, Berkeley
Colorado Department of Public Health, Denver
Connecticut State Department of Health, Hartford
Delaware Water Pollution Commission, Dover
Florida State Board of Health, Jacksonville
Florida State Board of Health, Miami
Florida State Board of Health, Pensacola
Florida State Board of Health, Winter Haven
Georgia Department of Public Health, Atlanta
Hawaii Department of Health, Laboratories Branch, Honolulu
Hawaii Department of Health, Occupational and Radiological Health
Section, Honolulu
Idaho Department of Health, Boise
Illinois Department of Air Pollution Control, Chicago
Illinois Department of Public Health, Springfield
Illinois Department of Public Health, State Sanitary Water Board,
Springfield
Illinois State Water Survey Division, Champaign
Illinois State Water Survey Division, Peoria
Indiana State Board of Health, Indianapolis
Iowa State Hygienic Laboratory, Des Moines
Iowa State Hygienic Laboratory, Iowa City
Kansas State Department of Health, Topeka
Kentucky State Department of Health, Division of Laboratory Services,
Frankfort
Kentucky State Department of Health, Public Health Laboratories Division,
Frankfort
Kentucky State Department of Health, Radiological Health Program,
Frankfort
Lawrence Experiment Station, Massachusetts

Louisiana State Board of Health, New Orleans
 Maryland State Department of Health, Baltimore
 Massachusetts Department of Public Health, Amherst
 Massachusetts Department of Public Health, Boston
 Michigan State Department of Health, Lansing
 Michigan Water Resources Commission, Lansing
 Minnesota Department of Health, Engineering Laboratories Section,
 Minneapolis
 Missouri Department of Public Health and Welfare, Jefferson City
 Montana Bureau of Mines and Geology, Butte
 Montana State Board of Health, Helena
 Nebraska Department of Agriculture and Economic Development, Lincoln
 Nebraska State Department of Health, Lincoln
 Nevada State Department of Health, Las Vegas
 Nevada State Department of Health, Reno
 New Hampshire Department of Health, Concord
 New Hampshire Water Pollution Commission, Concord
 New Jersey State Department of Health, Trenton
 New Jersey State Department of Health, Environmental Health Labor-
 atories, Trenton
 New Mexico Department of Public Health, Santa Fe
 New York State Air Pollution Control Board, Albany
 New York State Conservation Department, Oakdale, L.I.
 New York State Conservation Department, Scottsville
 New York State Department of Air Pollution Control, New York City
 New York State Department of Health, Albany
 North Carolina Department of Water Resources, Raleigh
 North Dakota State Department of Health, Bismarck
 Ohio Department of Agriculture, Reynoldsburg
 Ohio State Department of Health, Columbus
 Oklahoma State Health Department, Oklahoma City
 Oregon State Board of Health, Division of Sanitation and Engineering,
 Portland
 Pennsylvania Department of Agriculture, Harrisburg
 Pennsylvania Department of Health, Bureau of Air Pollution Control,
 Pittsburgh
 Pennsylvania Department of Health, Division of Air Pollution Control,
 Harrisburg
 Pennsylvania Department of Health, Division of Sanitary Engineering,
 Harrisburg
 Puerto Rico Aqueduct and Sewer Authority
 Puerto Rico Institute of Health Laboratories, Hato Rey
 Rhode Island State Department of Health, Providence
 South Carolina Department of Agriculture, Columbia
 South Carolina Pollution Control Authority, Columbia
 South Dakota Department of Health, Pierre
 Tennessee Department of Public Health, Division of Industrial Hygiene
 Service, Nashville

Tennessee Department of Public Health, Radiological Health Service,
 Nashville
 Tennessee Stream Pollution Control Board, Nashville
 Texas State Department of Health, Austin
 Utah State Department of Health, Salt Lake City
 Vermont Department of Water Resources, Montpelier
 Vermont State Department of Health, Barre
 Vermont State Public Health Laboratory, Burlington
 Virginia State Department of Health, Bureau of Industrial Hygiene,
 Richmond
 Virginia State Department of Health, Bureau of Laboratories, Richmond
 Virginia State Water Control Board, Richmond
 Washington State Department of Health, Seattle
 Washington State Food and Drug Laboratory, Seattle
 West Virginia Department of Natural Resources, Charleston
 Wisconsin Department of Agriculture, Madison
 Wisconsin State Laboratory of Hygiene, Madison

MUNICIPAL AGENCIES

Baltimore Health Department, Maryland
 Beaumont Health Department, Texas
 Bureau of Air Pollution Control and Heating Inspection, Cincinnati, Ohio
 Central District Filtration Plant, Chicago, Illinois
 Charlotte Water Department, North Carolina
 City of Allentown, Bureau of Water, Pennsylvania
 City of Amarillo, Texas
 City of Durham, Department of Water Resources, North Carolina
 City of Erie, Bureau of Water, Pennsylvania
 City of Los Angeles, Department of Water and Power, California
 City of Miami, Alexander Orr, Jr. Water Treatment Plant, Florida
 City of New York, Department of Health, New York
 City of New York, Department of Health, Food and Drug Laboratory,
 New York
 City of Niagara Falls, Division of Water Laboratories, New York
 City of Seattle, Washington
 City Water Department of Chattanooga, Tennessee
 City of Yonkers, Bureau of Water, New York
 Department of Health and Hospitals, St. Louis, Missouri
 Department of Public Works and Utilities, Flint, Michigan
 Department of Service and Buildings, Dayton, Ohio
 Eastern Pollution Control Center, Cleveland, Ohio
 Erie County Laboratory, Buffalo, New York
 Fresno Department of Public Health, California
 Houston Health Department, Texas
 Long Beach Water Department, California
 Los Angeles Air Pollution Control District, California
 Los Angeles County Air Pollution Control District, California

Los Angeles County Flood Control District, California
 Los Angeles County Sanitation District, Pomona, California (In cooperation with FWPCA)
 Los Angeles Department of Public Works, California
 Louisville Water Company, Kentucky
 Metropolitan St. Louis Sewer District, Missouri
 Metropolitan Sanitary District of Greater Chicago, Illinois
 Metropolitan Utilities District, Omaha, Nebraska
 Metropolitan Water District of Southern California, La Verne, California
 Minneapolis Water Department, Minnesota
 Monroe County Department of Health, Rochester, New York
 Nassau County Department of Health, Hempstead, New York
 Nassau County Department of Health, Mineola, New York
 Newburgh Water Department, New York
 North Jersey District Water Supply Commission, Wanaque
 Orange County Air Pollution Control District, Anaheim, California
 Pasadena Department of Public Health, California
 Philadelphia Department of Public Health, Environmental Health Laboratory, Pennsylvania
 Philadelphia Department of Public Health, Public Health Laboratory, Pennsylvania
 Philadelphia Suburban Water Company, Bryn Mawr, Pennsylvania
 Philadelphia Water Department, Pennsylvania
 Philadelphia Water Department, Belmont Laboratory, Pennsylvania
 Philadelphia Water Department, Torresdale Laboratory, Pennsylvania
 St. Louis County Water Company, Missouri
 Springwells Filtration Plant, Dearborn, Michigan
 Topeka Water Department, Kansas
 Water Pollution Control Board, Cincinnati, Ohio

FEDERAL AGENCIES

Associated Universities Incorporated, Brookhaven National Laboratory, Upton, Long Island, New York
 DHEW, Food and Drug Administration, Chicago, Illinois
 DHEW, Food and Drug Administration, Division of Pharmacology, Washington, D.C.
 DHEW, PHS, Air Pollution Technical Information Center, Division of Air Pollution, Washington, D.C.
 DHEW, PHS, Communicable Disease Center, Savannah, Georgia
 DHEW, PHS, Division of Dental Public Health, Bethesda, Maryland
 DHEW, PHS, Division of Environmental Engineering and Food Protection, Washington, D.C.
 DHEW, PHS, Information and Education Office, Division of Air Pollution, Washington, D.C.
 DHEW, PHS, Interstate Carrier Branch, Division of Environmental Engineering and Food Protection, Washington, D.C.
 DHEW, PHS, Northeast Shellfish Sanitation Research Center, Narragansett, Rhode Island

DHEW, PHS, Northeastern Radiological Health Laboratory, Winchester,
 Massachusetts
 DHEW, PHS, Radiological Health Laboratory, Rockville, Maryland
 DHEW, PHS, Regional Office IV, Atlanta, Georgia
 DHEW, PHS, Southeastern Radiological Health Laboratory, Montgomery,
 Alabama
 DHEW, PHS, Southwestern Radiological Health Laboratory, Las Vegas,
 Nevada
 District of Columbia Department of Public Health, Washington, D.C.
 Fourth U.S. Army Medical Laboratory, Fort Sam Houston, Texas
 Oak Ridge Institute of Nuclear Studies, Oak Ridge, Tennessee
 Pearl Harbor Naval Shipyard, Honolulu, Hawaii
 Regional Environmental Health Laboratory, McClellan AFB, California
 San Francisco Bay Naval Shipyard, Vallejo, California
 Sixth U.S. Army Medical Laboratory, Fort Baker, California
 Tennessee Valley Authority, Chattanooga, Tennessee
 Tennessee Valley Authority, Wilson Dam, Alabama
 2794th USAF Dispensary, Kelly AFB, Texas
 USAF Hospital (HWEBB), Wright Patterson AFB, Ohio
 U.S. Army Environmental Hygiene Agency, Edgewood Arsenal, Maryland
 U.S. Bureau of Sports, Fisheries, and Wildlife, Fish-Pesticide Research
 Laboratory, Denver, Colorado
 USDI, Bureau of Reclamation, Denver, Colorado
 USDI, FWPCA, Great Lakes-Illinois River Basins Project, Chicago,
 Illinois
 USDI, FWPCA, Ohio River Basin Project, Wheeling, West Virginia
 USDI, FWPCA, Pacific Northwest Water Laboratory, Corvallis, Oregon
 USDI, FWPCA, Technical Services Division, Washington, D.C.
 USDI, FWPCA, Water Quality Activities, Cincinnati, Ohio
 USDI, Geological Survey, Columbus, Ohio
 USDI, Geological Survey, Denver, Colorado
 USDI, Geological Survey, Little Rock, Arkansas
 USDI, Geological Survey, Philadelphia, Pennsylvania
 USDI, Geological Survey, Sacramento, California
 Walter Reed Army Medical Center, Washington, D.C.
 Water Pollution Control Federation, Washington, D.C.

FOREIGN AGENCIES

British Coke Research Association, Chesterfield, Derbyshire, England
 Central Electricity Research Laboratories, Leatherhead, Surrey, England
 City's Institute for Health Protection, Belgrade, Yugoslavia
 Comissao Inter-Municipal de Controle da Poluicao das Aguas E Do Ar,
 Sao Paulo, Brazil
 Department of Energy, Mines and Resources, Ottawa, Ontario, Canada
 Department of Health Services and Hospital Insurance, Vancouver, Canada
 Department of Municipal Laboratories, Hamilton, Ontario, Canada

Department of National Health and Welfare, Vancouver, Canada
 Department of National Health and Welfare, Occupational Health Division,
 Ottawa, Ontario, Canada
 Department of National Health and Welfare, Public Health Engineering
 Division, Ottawa, Ontario, Canada
 Instituto Nacional de Obras Sanitarias, Caracas, Venezuela
 Israel Institute of Technology, Haifa
 Metropolitan Corporation of Greater Winnipeg, Manitoba, Canada
 Metropolitan Water, Sewage, and Drainage Board, Sydney, Australia
 Ministere de la Sante, Montreal, Quebec, Canada
 National Institute of Hygienic Sciences, Tokyo, Japan
 National University of Colombia, Bogota
 Newcastle and Gateshead Water Company, Newcastle Upon Tyne, England
 Obras Sanitarias de la Nacion, Buenos Aires, Argentina
 Ontario Water Resources Commission, Toronto, Ontario, Canada
 Osaka City Institute of Hygiene, Japan
 Permutit Company, Limited, London, England
 Public Health Laboratory Service, London, England
 Scientific Research Council, Kingston, Jamaica, West Indies
 Taiwan Institute of Environmental Sanitation, Air Pollution and Radiolog-
 ical Health Section, Taipei, Taiwan, China
 Taiwan Institute of Environmental Sanitation, Division of Water Quality
 and Pollution Control, Taipei, Taiwan, China
 Taiwan Institute of Environmental Sanitation, PHA, Taiwan, China
 Taiwan Institute of Environmental Sanitation, Taichung Water Laboratory,
 Taichung, Taiwan, China
 Taiwan Institute of Environmental Sanitation, Tainan Water Laboratory,
 Tainan, Taiwan, China
 Taiwan Institute of Environmental Sanitation, Taitung Water Laboratory,
 Taitung, Taiwan, China
 Taiwan Institute of Environmental Sanitation, Training Section, Taipei,
 Taiwan, China
 United Kingdom Atomic Energy Authority, Didcot, Berks, England
 University of Beograd, Yugoslavia
 University of Leeds, England
 Waste Water Research Laboratory of the Swedish Forest Industries,
 Stockholm, Sweden
 Water Research Association, Marlow, Buckinghamshire, England

UNIVERSITIES

University of California, Richmond
 University of California, Riverside
 University of California, Engineering Material Laboratory, Berkeley
 University of California, Industrial Hygiene Engineering, Berkeley
 Clemson University, South Carolina
 Columbia University, Plainsboro, New Jersey

Cornell University, Ithaca, New York
 University of Dayton, Ohio
 Drexel Institute of Technology, Philadelphia, Pennsylvania
 Fairleigh Dickinson University, Madison, New Jersey
 University of Florida, College of Engineering, Gainesville
 Iowa State College, Ames
 University of Kansas, Lawrence
 Louisiana State University, Baton Rouge
 University of Minnesota, Minneapolis
 New York University Medical Center, New York
 University of North Carolina, Chapel Hill
 University of Pittsburgh, Pennsylvania
 Purdue University, Lafayette, Indiana
 Rensselaer Polytechnic Institute, Troy, New York
 Rutgers - The State University, Department of Agricultural Chemistry,
 New Brunswick, New Jersey
 Rutgers - The State University, Department of Environmental Science,
 New Brunswick, New Jersey
 St. Mary's College, Winona, Minnesota
 University of Vermont, Burlington
 Washington State University, Pullman

INDUSTRIES

American Bio-Chemical Laboratory, Baltimore, Maryland
 American Cyanamid Company, Wayne, New Jersey
 Anaconda Company, Grants, New Mexico
 Battelle Memorial Institute, Columbus, Ohio
 Bethlehem Steel Company, Bethlehem, Pennsylvania
 Bio-Technics Laboratories, Incorporated, Los Angeles, California
 Borg-Warner Corporation, Des Plaines, Illinois
 Brown and Caldwell Laboratories, San Francisco, California
 Calgon Corporation, Pittsburgh, Pennsylvania
 California Water Service Company, San Jose, California
 Chrysler Corporation, Detroit, Michigan
 Controls for Radiation Incorporated, Sandusky, Ohio
 Culligan Incorporated, Northbrook, Illinois
 Cyrus Wm. Rice and Company, Pittsburgh, Pennsylvania
 Dow Chemical, Midland, Michigan
 E.I. du Pont de Nemours and Company, Aiken, South Carolina
 Ekroth Laboratories, Incorporated, Brooklyn, New York
 Emery Industries, Incorporated, Cincinnati, Ohio
 FMC Corporation, Pocatello, Idaho
 Fairbanks, Morse and Company Research Center, Beloit, Wisconsin
 General Electric Company, Louisville, Kentucky
 Good Year Atomic Corporation, Piketon, Ohio
 H.C. Nutting Company, Cincinnati, Ohio
 Hammond-Montel, Incorporated, Elmhurst, New York

Havens-Emerson, Oradell, New Jersey
 Hazleton Nuclear Science Corporation, Palo Alto, California
 Holzmacher, McLendon and Murrell, Melville, New York
 Industrial Chemicals, Incorporated, South Bend, Indiana
 INFILCO, General American Transportation Corporation, Tucson, Arizona
 Ionics, Incorporated, Watertown, Massachusetts
 Johns-Manville Research and Engineering Center, Manville, New Jersey
 Kem-Tech Laboratories, Incorporated, Baton Rouge, Louisiana
 Kennecott Copper Corporation, Salt Lake City, Utah
 Magnus Chemical, Garwood, New Jersey
 Mallinckrodt Chemical Works, St. Louis, Missouri
 Maryland Cooperative Milk Producers, Incorporated, Baltimore, Maryland
 McCrone Associate, Incorporated, Chicago, Illinois
 Midwest Research Institute, Kansas City, Missouri
 Minute Maid Company, Anaheim, California
 Monsanto Company, St. Louis, Missouri
 NALCO Chemical Company, Chicago, Illinois
 New Mexico Institute of Mining and Technology, Socorro
 Nuclear-Chicago Corporation, Des Plaines, Illinois
 Pacific Gas and Electric Company, Emeryville, California
 Pacific Gas and Electric Company, San Francisco, California
 Pan American World Airways, Patrick Air Force Base, Florida
 Pomeroy, Johnston and Bailey, Pasadena, California
 Radiation Applications, Incorporated, Long Island, New York
 Radiation Detection Company, Mountain View, California
 Ray W. Hawksley Company, Incorporated, Richmond, California
 Reynolds Electrical and Engineering Company, Incorporated, Industrial
 Hygiene, Las Vegas, Nevada
 Reynolds Electrical and Engineering Company, Incorporated, Radiological
 Sciences Department, Las Vegas, Nevada
 Roy F. Weston, Incorporated, West Chester, Pennsylvania
 Sandia Corporation, Albuquerque, New Mexico
 Shell Chemical Company, Princeton, New Jersey
 Southern Testing and Research Laboratories, Incorporated, Wilson,
 North Carolina
 Tracerlab, Incorporated, Richmond, California
 U.S. Industrial Chemicals Company, Tuscola, Illinois
 W.R. Grace and Company, Dearborn Chemical Division, Lake Zurich,
 Illinois
 Wastewater Analysis Corporation, Lincoln Park, Michigan
 Water Service Laboratories, Incorporated, New York, New York
 York Research Corporation, Stamford, Connecticut